<table>
<thead>
<tr>
<th>Date Due</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sep 24, 1951</td>
</tr>
<tr>
<td>May 4, 1954</td>
</tr>
<tr>
<td>Apr 1, 1955</td>
</tr>
<tr>
<td>Dec 16, 1958</td>
</tr>
<tr>
<td>1962</td>
</tr>
<tr>
<td>1962</td>
</tr>
<tr>
<td>1962</td>
</tr>
</tbody>
</table>
TEXT-BOOKS OF INORGANIC CHEMISTRY


A TEXT-BOOK OF
INORGANIC CHEMISTRY.

EDITED BY
J. NEWTON FRIEND, D.Sc., F.I.C., PH.D.
Carnegie Gold Medallist.


PART II. The Inert Gases (Group 0 in the Periodic Table). By H. V. A. Briscoe, D.Sc. (Lond.), A.R.C.S.

PART III. The Alkali Metals and their Congeners (Group I of the Periodic Table). By A. Jamieson Walker, Ph.D. (Hild.).

PART IV. The Alkaline Earth Metals and their Associates (Group II of the Periodic Table). By H. V. A. Briscoe, D.Sc. (Lond.), A.R.C.S., and E. Sinkinson.

PART V. Aluminium and its Congeners, including the Rare Earth Metals (Group III of the Periodic Table). By H. F. V. Little, B.Sc. (Lond.), A.R.C.S., Chief Chemist to Thorium Ltd.

PART VI. Carbon and its Allies (Group IV of the Periodic Table). By R. M. Caven, D.Sc. (Lond.), F.I.C.

PART VII. Nitrogen and its Congeners (Group V of the Periodic Table). By J. C. Withers, Ph.D. (Würz.), and H. F. V. Little, B.Sc. (Lond.), A.R.C.S., Chief Chemist to Thorium Ltd.

PART VIII. Sulphur and its Congeners (Group VI of the Periodic Table). By Douglas F. Twiss, D.Sc. (B'ham.), F.I.C., and Arthur V. Eldridge, B.Sc. (Lond.), F.I.C.

PART IX. The Halogens and their Allies (Group VII of the Periodic Table). By Geoffrey Martin, D.Sc., Ph.D., and Ernest A. Dancaster, B.Sc. (Lond.).


PART XII. The Metal Ammines, with a General Introduction to the Theory of Complex Inorganic Substances. By H. F. V. Little, B.Sc.

<table>
<thead>
<tr>
<th>Periods</th>
<th>Group 0</th>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
<th>Group IV</th>
<th>Group V</th>
<th>Group VI</th>
<th>Group VII</th>
<th>Group VIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>First short period</td>
<td>He 4:00</td>
<td>H 1:008</td>
<td>Li 6:94</td>
<td>Li 6:94</td>
<td>Li 6:94</td>
<td>Li 6:94</td>
<td>Li 6:94</td>
<td>Li 6:94</td>
<td>Li 6:94</td>
</tr>
<tr>
<td>Second short period</td>
<td>Na 20:2</td>
<td>Na 23:00</td>
<td>Mg 24:32</td>
<td>Al 27:1</td>
<td>Si 28:3</td>
<td>P 31:04</td>
<td>S 32:06</td>
<td>Cl 35:46</td>
<td></td>
</tr>
<tr>
<td>First long period</td>
<td>A 39:88</td>
<td>K 39:10</td>
<td>Ca 40:07</td>
<td>Sc 44:1</td>
<td>Ti 48:1</td>
<td>V 51:0</td>
<td>Cr 52:0</td>
<td>Mn 54:93</td>
<td>Fe 55:84</td>
</tr>
<tr>
<td>Odd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second long period</td>
<td>Kr 82:9</td>
<td>Rb 85:45</td>
<td>Sr 87:63</td>
<td>Y 88:7</td>
<td>Zr 90:6</td>
<td>Nb 93:1</td>
<td>Mo 96:0</td>
<td>Ru 101:7</td>
<td>Rh 102:9</td>
</tr>
<tr>
<td>Even series</td>
<td>Ag 107:88</td>
<td>Cd 112:4</td>
<td>In 114:8</td>
<td>Sn 118:7</td>
<td>Sb 120:2</td>
<td>Te 127:5</td>
<td>I 126:92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Third long period</td>
<td>Xe 130:2</td>
<td>Cs 132:81</td>
<td>Ba 137:37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Even series</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fourth long period</td>
<td>Au 197:2</td>
<td>Hg 200:6</td>
<td>Tl 204:0</td>
<td>Pb 207:20</td>
<td>Bi 208:0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Even series</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fifth long period</td>
<td>Nt 222:4</td>
<td>Ra 226:0</td>
<td>Th 232:4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formulas of oxides</td>
<td>R₂O</td>
<td>RO</td>
<td>R₂O₃</td>
<td>RO₃</td>
<td>R₂O₅</td>
<td>R₂O₇</td>
<td>R₂O₉</td>
<td>RO₄</td>
<td></td>
</tr>
<tr>
<td>Formulas of hydrides</td>
<td>RH</td>
<td>RH₂</td>
<td>RH₃</td>
<td>RH₄</td>
<td>RH₅</td>
<td>RH₆</td>
<td>RH₇</td>
<td>RH₈</td>
<td></td>
</tr>
<tr>
<td>Volume in this series of text-books</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
</tr>
</tbody>
</table>

* The International Atomic Weights for 1918 are adopted in this Table.
A TEXT-BOOK OF INORGANIC CHEMISTRY

EDITED BY
J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C.
CARNEGIE GOLD MEDALLIST

VOLUME IX. PART I

COBALT, NICKEL, AND THE ELEMENTS OF THE PLATINUM GROUP

BY
J. NEWTON FRIEND
HON. CAPTAIN ROYAL ENGINEERS

LONDON
CHARLES GRIFFIN AND COMPANY, LIMITED
PHILADELPHIA: J. B. LIPPINCOTT COMPANY
1920
[All rights reserved]
GENERAL INTRODUCTION TO THE SERIES

DURING the past few years the civilised world has begun to realise the advantages accruing to scientific research, with the result that an ever-increasing amount of time and thought is being devoted to various branches of science.

No study has progressed more rapidly than chemistry. This science may be divided roughly into several branches: namely, Organic, Physical, Inorganic, and Analytical Chemistry. It is impossible to write any single text-book which shall contain within its two covers a thorough treatment of any one of these branches, owing to the vast amount of information that has been accumulated. The need is rather for a series of text-books dealing more or less comprehensively with each branch of chemistry. This has already been attempted by enterprising firms, so far as physical and analytical chemistry are concerned; and the present series is designed to meet the needs of inorganic chemists. One great advantage of this procedure lies in the fact that our knowledge of the different sections of science does not progress at the same rate. Consequently, as soon as any particular part advances out of proportion to others, the volume dealing with that section may be easily revised or rewritten as occasion requires.

Some method of classifying the elements for treatment in this way is clearly essential, and we have adopted the Periodic Classification with slight alterations, devoting a whole volume to the consideration of the elements in each vertical column, as will be evident from a glance at the scheme in the Frontispiece.

In the first volume, in addition to a detailed account of the Elements of Group 0, the general principles of Inorganic Chemistry are discussed. Particular pains have been taken in the selection of material for this volume, and an attempt has been made to present to the reader a clear account of the principles upon which our knowledge of modern Inorganic Chemistry is based.

At the outset it may be well to explain that it was not intended to write a complete text-book of Physical Chemistry. Numerous excellent works have already been devoted to this subject, and a volume on such lines would scarcely serve as a suitable introduction to this series. Whilst Physical Chemistry deals with the general principles applied to all branches of theoretical chemistry, our aim has been to emphasise their application to Inorganic Chemistry, with which branch of the subject this series of text-books is exclusively concerned. To this end practically all the illustrations to the laws and principles discussed in Volume I deal with inorganic substances.

Again, there are many subjects, such as the methods employed in the accurate determination of atomic weights, which are not generally regarded as forming part of Physical Chemistry. Yet these are sub-
jects of supreme importance to the student of Inorganic Chemistry, and are accordingly included in the Introduction.

Hydrogen and the ammonium salts are dealt with in Volume II, along with the Elements of Group I. The position of the rare earth metals in the Periodic Classification has for many years been a source of difficulty. They have all been included in Volume IV, along with the Elements of Group III, as this was found to be the most suitable place for them.

Many alloys and compounds have an equal claim to be considered in two or more volumes of this series, but this would entail unnecessary duplication. For example, alloys of copper and tin might be dealt with in Volumes II and V respectively. Similarly, certain double salts—such, for example, as ferrous ammonium sulphate—might very logically be included in Volume II under ammonium, and in Volume IX under iron. As a general rule this difficulty has been overcome by treating complex substances, containing two or more metals or bases, in that volume dealing with the metal or base which belongs to the highest group of the Periodic Table. For example, the alloys of copper and tin are detailed in Volume V along with tin, since copper occurs earlier, namely, in Volume II. Similarly, ferrous ammonium sulphate is discussed in Volume IX under iron, and not under ammonium in Volume II. The ferro-cyanides are likewise dealt with in Volume IX.

But even with this arrangement it has not always been found easy to adopt a perfectly logical line of treatment. For example, in the chromates and permanganates the chromium and manganese function as part of the acid radicles and are analogous to sulphur and chlorine in sulphates and perchlorates; so that they should be treated in the volume dealing with the metal acting as base, namely, in the case of potassium permanganate, under potassium in Volume II. But the alkali permanganates possess such close analogies with one another that separate treatment of these salts hardly seems desirable. They are therefore considered in Volume VIII.

Numerous other little irregularities of a like nature occur, but it is hoped that, by means of carefully compiled indexes and frequent cross-referencing in the texts of the separate volumes, the student will experience no difficulty in finding the information he requires.

Particular care has been taken with the sections dealing with the atomic weights of the elements in question. The figures given are not necessarily those to be found in the original memoirs, but have been recalculated, except where otherwise stated, using the following fundamental values:

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.00762</td>
</tr>
<tr>
<td>Sodium</td>
<td>22.996</td>
</tr>
<tr>
<td>Potassium</td>
<td>39.100</td>
</tr>
<tr>
<td>Silver</td>
<td>107.880</td>
</tr>
<tr>
<td>Carbon</td>
<td>12.011</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>14.008</td>
</tr>
<tr>
<td>Oxygen</td>
<td>16.000</td>
</tr>
<tr>
<td>Sulphur</td>
<td>32.065</td>
</tr>
<tr>
<td>Fluorine</td>
<td>19.015</td>
</tr>
<tr>
<td>Chlorine</td>
<td>35.457</td>
</tr>
<tr>
<td>Bromine</td>
<td>79.916</td>
</tr>
<tr>
<td>Iodine</td>
<td>126.904</td>
</tr>
</tbody>
</table>

By adopting this method it is easy to compare directly the results of earlier investigators with those of more recent date, and moreover it renders the data for the different elements strictly comparable throughout the whole series.

Our aim has not been to make the volumes absolutely exhaustive,
as this would render them unnecessarily bulky and expensive; rather has it been to contribute concise and suggestive accounts of the various topics, and to append numerous references to the leading works and memoirs dealing with the same. Every effort has been made to render these references accurate and reliable, and it is hoped that they will prove a useful feature of the series. The more important abbreviations, which are substantially the same as those adopted by the Chemical Society, are detailed in the subjoined list.

In order that the series shall attain the maximum utility, it is necessary to arrange for a certain amount of uniformity throughout, and this involves the suppression of the personality of the individual author to a corresponding extent for the sake of the common welfare. It is at once my duty and my pleasure to express my sincere appreciation of the kind and ready manner in which the authors have accommodated themselves to this task, which, without their hearty co-operation, could never have been successful. Finally, I wish to acknowledge the unfailing courtesy of the publishers, Messrs. Charles Griffin and Co., who have done everything in their power to render the work straightforward and easy.

J. NEWTON FRIEND

October 1919
PREFACE

In the preparation of Volume IX it has been found desirable to depart somewhat from the plan adopted in the other volumes of this Series. Thus, the study of iron is relegated to Part II, whereas, if the logical sequence had been maintained, the metal would have received treatment before cobalt and nickel. Owing to the importance of iron, and the enormous amount of research that has been carried out in connection with its properties and those of its compounds, it was felt that the subject deserved a separate book, and Part II of this volume has accordingly been assigned to it.

Again, the platinum metals are so closely similar in many of their properties that it was decided to treat of their detection and estimation all together in Chapter X, rather than to deal with each separately at the end of the chapters dealing with their compounds, as has been done with cobalt and nickel, and, indeed, with the elements in the remaining volumes.

The state of our knowledge of the chemistry of the platinum metals, although greatly improved during the last twenty years, is still far from satisfactory. This, no doubt, is due to a variety of reasons, such as the rarity of the metals, their consequently high cost, and their similarity to one another, which renders their preparation in a state of purity an extremely arduous task. This latter feature is well exemplified by the efforts of Matthey to prepare pure iridium. His work is described in fair detail on pp. 235-286 of the text. Even after a most elaborate treatment the metal still contained traces of ruthenium and rhodium.

In consequence of this difficulty, there can be no doubt that the early investigators frequently worked with a very impure metal, and this may in some measure account for discrepancies and apparent contradictions in their results.

Again, imperfect methods of analysis frequently led the investigator of last century astray, so that he was led to postulate the existence of many compounds, some of which have since been proved to be mixtures. Thus, for example, Claus, in 1846, observed that when ruthenium is heated to a high temperature in air a bluish black mass of oxide is formed, corresponding in chemical composition to the formula RuO₂. Accordingly, the existence of this compound was accepted as proven until 1905, when Guttber showed that the product is probably a mixture of ruthenium and its di-oxide, RuO₂. No doubt many other substances, supposedly compounds, are really mixtures. In cases where reasonable doubt exists, the present author has given indications in the text for the guidance of the reader.

Attention may, in this connection, be called to the desirability of extending our knowledge of the chemistry of the platinum metals. Only a few modern chemists, and those mostly German, have attacked the
The story of the success attending these chemists in the very limited number of researches undertaken reads almost like a romance, and should stimulate British workers seeking promising fields for research.

Thus, for example, prior to 1913 no definite fluoride of osmium had been isolated, although it was known that combination could take place between fluorine and osmium. In that year, however, Ruff and Tschirch, in a fascinating memoir, described the preparation and isolation of a complete series of fluorides, namely, $\text{OsF}_8$, $\text{OsF}_6$, and $\text{OsF}_4$. Evidence was also obtained that the tetrafluoride could combine with alkali fluorides to form fluorosmates, of general formula $\text{M}_2\text{OsF}_6$, analogous to the better known chlorosmates and chlorplatinates.

As an example of another kind of research may be mentioned that of Levy, who has demonstrated that certain hydrated platino cyanides can exist in two modifications, having the same crystalline form and chemical composition, but exhibiting a remarkable difference in their optical properties.

In view of the foregoing it seems certain that discoveries of the highest interest are awaiting the diligent research student in this particular field.

For the research student fuller details are necessary than can be given in a text-book of this kind. This difficulty is to some degree met by copious references to original literature, so that a student who has access to a suitable library may acquire the information he needs with the maximum rapidity. In this connection it may be mentioned that in almost every case the original memoir has been consulted in the Library of the Chemical Society by the present author, and although it is too much to hope that the references are entirely free from error, it is believed that any such errors will be few and of minor importance.

In preparing a work of this kind it is a great advantage for an author to receive constructive criticism and advice from his friends. My sincerest thanks are due to Dr. Caven and to Mr. Little, who have carefully read through the whole of the work in proof, and made numerous alterations, additions, and suggestions. In addition to this, Mr. Little very kindly wrote the sections on the atomic weights of the metals. Through the kindness of Mr. Clifford, the courteous Librarian of the Chemical Society, it has been possible for me to gain access to many early memoirs in a manner that would otherwise have been quite out of the question. My thanks are due also to Messrs. W. R. Barclay, A. Banks, A. V. Eldridge, B.Sc., and to many other gentlemen for kind assistance in one way or another.

J. N. F.

October 1919
CONTENTS

THE PERIODIC TABLE (Frontispiece) iv
GENERAL INTRODUCTION TO THE SERIES vii
PREFACE xi
LIST OF ABBREVIATIONS xv

CHAPTER I. General Characteristics of the Elements of Group VIII

The Grouping of Elements into Triads—Atomic Weights of the Elements—

CHAPTER II. Cobalt and its Compounds


CHAPTER III. Nickel and its Compounds


CHAPTER IV. Ruthenium and its Compounds


CHAPTER V. Rhodium and its Compounds


CHAPTER VI. Palladium and its Compounds


CHAPTER VII. Osmium and its Compounds


CHAPTER VIII. Iridium and its Compounds


CHAPTER IX. Platinum and its Compounds


CHAPTER X. Detection and Estimation of the Platinum Metals


NAME INDEX

SUBJECT INDEX
## LIST OF CHIEF ABBREVIATIONS EMPLOYED IN THE REFERENCES

<table>
<thead>
<tr>
<th>Abbreviated Title</th>
<th>Journal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amer. Chem. J.</td>
<td>American Chemical Journal.</td>
</tr>
<tr>
<td>Analyst</td>
<td>The Analyst.</td>
</tr>
<tr>
<td>Annalen</td>
<td>Justus Lихиг's Annalen der Chemie.</td>
</tr>
<tr>
<td>Arch. Pharm.</td>
<td>Archiv der Pharmazie.</td>
</tr>
<tr>
<td>B.A. Reports</td>
<td>British Association Reports.</td>
</tr>
<tr>
<td>Centr. Min.</td>
<td>Centralblatt für Mineralogie.</td>
</tr>
<tr>
<td>Chem. Zeit.</td>
<td>Chemiker Zeitung (Gothen).</td>
</tr>
<tr>
<td>Crell's Annalen</td>
<td>Chemische Annalen für die Freunde der Naturlehre, von L. Crolle.</td>
</tr>
<tr>
<td>Dingl. poly. J.</td>
<td>Dingler's polytechnisches Journal.</td>
</tr>
<tr>
<td>Drude's Annalen</td>
<td>Annalen der Physik (1900–1906).</td>
</tr>
</tbody>
</table>

**VOL. IX: I**
### LIST OF CHIEF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviated Title</th>
<th>Journal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eng. and Min. J.</td>
<td>Engineering and Mining Journal.</td>
</tr>
<tr>
<td>Gazzetta</td>
<td>Gazzetta chimica italiana.</td>
</tr>
<tr>
<td>Gilbert's Annalen</td>
<td>Annalen der Physik (1799-1824).</td>
</tr>
<tr>
<td>J. Geol.</td>
<td>Journal of Geology.</td>
</tr>
<tr>
<td>J. Physical Chem.</td>
<td>Journal de Physique.</td>
</tr>
<tr>
<td>J. Physique</td>
<td>Journal für Physik.</td>
</tr>
<tr>
<td>Mon. scient.</td>
<td>Monitor scientifique.</td>
</tr>
<tr>
<td>Monatsh.</td>
<td>Monatshfte für Chemie und verwandte Theile anderer Wissenschaften.</td>
</tr>
<tr>
<td>Pflüger's Archiv.</td>
<td>Archiv für die gesammte Physiologie des Menschen und der Thiere.</td>
</tr>
<tr>
<td>Pharm. Zentr.-h.</td>
<td>Pharmazeutische Centralblatt.</td>
</tr>
<tr>
<td>Pharm. Post</td>
<td>Pharmazeutische Post.</td>
</tr>
<tr>
<td>Phil. Trans.</td>
<td>Philosophical Transactions of the Royal Society of London.</td>
</tr>
<tr>
<td>Amsterdam</td>
<td></td>
</tr>
<tr>
<td>Roy. Inst. Reports</td>
<td>Reports of the Royal Institution.</td>
</tr>
<tr>
<td>Schweiger's J.</td>
<td>Journal für Chemie und Physik.</td>
</tr>
</tbody>
</table>
LIST OF CHIEF ABBREVIATIONS

ABBREVIATED TITLE. JOURNAL.
Sitzungsber. K. Akad. Wiss. Sitzungsberichte der Königlich bayerischen Akademie
der Wissenschaften zu Wien.
Techn. Jahresber. Jahresbericht über die Leistungen der Chemischen
Soc. Transactions of the Chemical Society.
et Mesures.
Aerzte und Aerzte.
Wied. Annalen Wiedermann's Annalen der Physik und Chemie (1877–
Zeitschrift für physiologische Chemie.
Wissenschaftl. Abhandl. Wissenschaftliche Abhandlungen der physikalisch-tech-
phys.-tech. Reichsanst. nischen Reichsanstalt.
Zeitsch. Chem. Ind. Kolloide. Zeitschrift für Chemie und Industrie des Kolloide (con-
Zeitsch. Nähr. Genuss-m. Zeitschrift für Untersuchung der Nahrungs-und Genuss-
mittel.
Zeitsch. physikal. Chem. Zeitschrift für physikalische Chemie, Stöchiometrie und
Verwandtschaftslehre.
Zeitsch. wiss. Photochem. Zeitschrift für wissenschaftliche Photographie, Photo-
physik, und Photochemie.
As long ago as the beginning of last century the attention of chemists had been drawn to the fact that certain triads of elements exist which exhibit not only a close similarity in their chemical and physical properties, but also an interesting regularity in their atomic weights.\(^1\) For several years, however, the subject was allowed to drop into abeyance until Dumas, in 1851, again brought it to the fore,\(^2\) and both he and other chemists rapidly added to the list of regularities. At first it was hoped that all the elements might ultimately be grouped into triads, and that in this way a complete system of classifying the elements might be evolved, inasmuch as the Periodic Classification had not as yet been introduced. These hopes were, however, doomed to failure, and a severe blow was struck at the utility of the triads when Cooke\(^3\) showed that some of them actually broke into natural groups of elements. The halogens are a case in point, for chlorine, bromine, and iodine are but three out of four closely similar elements, and no system of classification that deals with these to the exclusion of fluorine can be regarded as satisfactory. A similar objection applies to the triad of alkali metals, namely, lithium, sodium, and potassium, for whilst it is true that they resemble each other very closely, a remarkable analogy likewise exists between them and rubidium and caesium, the five elements thus constituting a natural pentadic group.

As already stated, the majority of the triads exhibit an interesting relationship between the numerical values of their atomic weights, the mean of the first and third being almost identical with the middle

\(^1\) Doebereiner, Gilbert's Annalen, 1817, 57, 436; Pogg. Annalen, 1829, 15, 301. See also Gilbert's Annalen, 1816, 56, 332, which contains a report by Wurzer on Doebereiner.

\(^2\) Dumas, British Assoc. Reports, 1851; Compt. rend., 1857, 45, 709; 1858, 46, 961; 1858, 47, 1026.

\(^3\) J. P. Cooke, Amer. J. Sci., 1854, 17, 387.
value. Thus, in the case of the halogen and alkali triads respectively, the figures are given in the accompanying table:

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic weight</th>
<th>Difference</th>
<th>Mean of extreme atomic weights</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>6.94</td>
<td>16.06</td>
<td>23.02</td>
</tr>
<tr>
<td>Sodium</td>
<td>23.00</td>
<td>16.10</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>35.46</td>
<td>44.46</td>
<td>81.19</td>
</tr>
<tr>
<td>Chlorine</td>
<td>126.92</td>
<td>47.00</td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td>79.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodine</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Three sets of triads exist, however, which do not exhibit this relationship; indeed their atomic weights closely approximate to one another. Furthermore, by arranging these elements in the form of triads no natural groups are broken into, since the triads appear to be complete and self-contained. They are as follow:

1. Iron 55.84  2. Ruthenium 101.7  3. Osmium 190.9
   Cobalt 58.97  Rhodium 102.9  Iridium 193.1
   Nickel 58.68  Palladium 106.7  Platinum 195.2

Not only do the elements in each of the above triadic groups exhibit a more or less regular gradation in their properties, but a certain amount of similarity is found to exist between a member of any one triad and the corresponding members of the other triads. Thus, for example, iron, ruthenium, and osmium have several interesting peculiarities in common; so have cobalt, rhodium, and iridium, as well as nickel, palladium, and platinum.

Such relationships between three sets of triads are unique, and no systematic classification of the elements can afford to ignore them.

After the enunciation of the Law of Octaves by Newlands in 1864, and the realisation by chemists that a convenient method of grouping the elements could indeed be obtained by arranging them in the order of increasing atomic weights, the nine elements mentioned above were given a unique position in a group by themselves, namely, in the eighth vertical column of the Periodic Table (see Frontispiece). The remarkable feature of this grouping lies in the fact that whilst in every other vertical column save that apportioned to the Rare Earth Metals only one single element occupies the position in each horizontal series,¹ in the eighth group those positions are occupied by triads. It will be observed that these triads occupy intermediate positions between the even and odd series of the First, Second, and Fourth Long Periods respectively. For this reason they are termed the transitional elements, and, as will be seen later, their chemical properties justify their position as intermediaries between the metals of the even and odd series of the seventh and first groups respectively.

¹ Excluding most of the radio-elements derived from thorium and uranium.
The Atomic Weights of the Elements of Group VIII

It will be observed that cobalt is placed between iron and nickel in the Periodic Table figured on the Frontispiece, although its atomic weight (58.97) is greater than that of nickel (58.68). This is one of the anomalies of the scheme which still awaits solution. Nickel resembles palladium and platinum far more closely than it does rhodium and iridium, whilst the reverse is true for cobalt. Hence it may be inferred that, despite the irregularity in the atomic weights, the true position of nickel is at the end of the triadic group, and that of cobalt is the centre. This receives strong support from the fact that by placing cobalt between iron and nickel a more gradual variation in the properties of the three elements becomes observable. This will be made abundantly evident in the sequel. In 1870 a similar difficulty confronted chemists in connection with osmium, iridium, and platinum, which were believed to have the following atomic weights:

- Osmium: 198.6
- Iridium: 196.7
- Platinum: 195.2

According to this their positions in Group VIII should be reversed, platinum appearing in the same vertical line as iron and ruthenium, osmium being relegated to the end of the triadic group, namely, under nickel and palladium. Such an arrangement, however, is opposed to the general properties of these elements, platinum resembling nickel and palladium more closely than it does iron and ruthenium, the reverse being true for osmium. Subsequent research has shown, however, that the atomic weights assigned to the elements in question in 1870 were incorrect. The values recognised by the International Atomic Weight Committee for 1918 are as follow:

- Osmium: 190.9
- Iridium: 193.1
- Platinum: 195.2

This brings the three elements into complete harmony with the general scheme. It is always possible that further research may ultimately prove, in a similar manner, that nickel and cobalt are not real, but only apparent, exceptions to the Periodic Law. It must be admitted, however, that this is very unlikely, since it necessitates either very considerable errors in the modern determinations of their atomic weights, or the assumption that one or both of these elements is in reality complex.

The most recent views on the Periodic Classification suggest an entirely different method of removing the anomaly, namely, that the atomic weight is not the correct property to use in arranging the elements; rather should one be chosen which increases by a constant amount in passing from one element to the next. Physical theory indicates the positive nuclear charge of the atom to be one such property, whilst experimentally it is found that the X-ray spectra afford such a property, and eliminate the nickel-cobalt anomaly.1

---

General Properties of the Metals of Group VIII

The general physical properties of the metals are given in tabular form on the facing page, and a strong family likeness may be traced throughout the whole group. Thus in general appearance they are silver white, remaining bright in dry air. In their behaviour towards moist air one metal, namely, iron, is unique. It readily corrodes, yielding a brown pulverulent mass of hydrated oxide known familiarly as rust. The other metals either simply tarnish or remain entirely unaffected.

When in a state of fine division several of the metals exhibit powerful catalysing properties. For example, platinum black introduced into hydrogen and oxygen mixed in the proportions necessary to form water, causes the two gases to unite with a loud explosion; whilst nickel is used commercially in a finely divided condition for effecting the hardening or hydrogenation of unsaturated oils, such as linseed and cotton-seed oils.

The temperatures at which the metals begin to volatilise in vacuo to a detectable extent are of the same order. The following data have been given 1:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>640</td>
</tr>
<tr>
<td>Iridium</td>
<td>660</td>
</tr>
<tr>
<td>Palladium</td>
<td>735</td>
</tr>
<tr>
<td>Iron</td>
<td>755</td>
</tr>
</tbody>
</table>

The metals melt and boil at very high temperatures, the melting-points ranging from 1500° C. upwards, and the boiling-points lying in the neighbourhood of 2500° C. For this reason several of them, such as platinum and its alloys, irido-platinum, etc., are employed in the manufacture of crucibles and scientific apparatus destined for use at high temperatures. Iron and nickel are used commercially in the construction of machinery and mechanical appliances liable to exposure to extremes of heat.

The metals are further characterised by their power of forming complex radicles with other elements or groups. Well-known examples are the ferro-cyanides, osmo-cyanides, pallado-cyanides, etc., in which the metals, combined with the cyanogen group, yield complex negative radicles with properties entirely different from those characteristic of the ordinary metallic salts. Most of the metals yield remarkable series of complex ammino derivatives, of which the best known are the cobaltammines and platinammines.

Into a somewhat similar category must be placed the double halogenides such as chlor-ruthenates and chlor-platinates; double nitrites like those of cobalt, rhodium, and osmium; and the double oxides, as exemplified by the ferrates, osmates, and ruthenates.

An interesting series of salts is afforded by the alums of trivalent iron, cobalt, rhodium, and iridium. These have the general formula

\[ \text{M}_n\text{SO}_4\cdot \text{R}_2\text{(SO}_4)_3\cdot 24\text{H}_2\text{O} \]

are isomorphous, and establish a link between the foregoing elements and aluminium, chromium, and manganese.

Despite these and other analogies between the nine elements of Group VIII, it is not difficult to observe that the six elements of greatest

1 Knooko, *Ber.*, 1909, 42, 206. Knooko gives 540° C. for platinum, but Roberts (Phil. Mag., 1913, 25, 270) showed the metal does not volatilise in vacuo.
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic weight</th>
<th>Mean specific heat (0–100°C)</th>
<th>Mean atomic heat</th>
<th>Melting-point, °C.</th>
<th>Boiling-point, °C.</th>
<th>Density</th>
<th>Coefficient of expansion</th>
<th>Order of volatility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>195.2</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Iridium</td>
<td>193.1</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Osmium</td>
<td>190.9</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Palladium</td>
<td>106.7</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Rhodium</td>
<td>102.9</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>101.7</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Nickel</td>
<td>58.7</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Cobalt</td>
<td>59.0</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Iron</td>
<td>55.8</td>
<td>0.0028</td>
<td>9.6</td>
<td>1950</td>
<td>3160</td>
<td>1.25</td>
<td></td>
<td>4</td>
</tr>
</tbody>
</table>

Notes:
- 8.8 rolled
- 8.8 cast
- 0.02328
atomic weight exhibit a much closer similarity amongst themselves than towards iron, cobalt, and nickel. Their melting-points and coefficients of expansion with rise of temperature are of the same order; they are readily reduced to the metallic condition from their compounds, and generally speaking manifest considerable resistance towards acids and the usual chemical reagents.

A characteristic property of the platinum metals consists in the readiness with which they admit of being prepared in the colloidal state as hydrosols. These latter possess powerful catalytic properties, and their accelerating influence upon the rate of decomposition of aqueous solutions of hydrogen peroxide has been carefully studied. The most powerful catalyst is colloidal osmium, followed in order of decreasing activity by platinum, palladium, and iridium.1

The hydrosols are more active than their respective metals in finely divided condition; this is attributable to their increased surface and to the more intimate contact between the particles of metal and the molecules to be catalytically acted upon.

Hydrogen, in the presence of these hydrosols, exhibits increased activity. For example, when this gas is passed into a mixture consisting of

10 c.c. of metallic hydrosol
10 c.c. of alcohol
2 grs. of nitrobenzene

the last-named substance is reduced to aniline:

\[ \text{C}_6\text{H}_5\text{NO}_2 + 3\text{H}_2 = \text{C}_6\text{H}_5\text{NII}_2 + 2\text{H}_2\text{O}. \]

By measuring the volumes of hydrogen utilised in this way in unit time per unit volume of metallic hydrosol, a measure of the relative efficiencies of the colloidal metals is obtained. The results obtained by Paal and his co-workers are as follow:

<table>
<thead>
<tr>
<th></th>
<th>c.c. hydrogen per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium hydrosol</td>
<td>12,000 to 32,000</td>
</tr>
<tr>
<td>Platinum</td>
<td>6,700 to 37,000</td>
</tr>
<tr>
<td>Iridium</td>
<td>2,000 to 4,000</td>
</tr>
<tr>
<td>Osmium</td>
<td>Only small activity</td>
</tr>
</tbody>
</table>

There is little to choose between palladium and platinum, whilst the activity of osmium is exceedingly small.

Several of the metals yield solid hydrosols when their solutions are concentrated in the presence of a protective colloid, such as gum acacia or sodium lysalbinate, over concentrated sulphuric acid in vacuo. On treatment with warm water the solids redissolve, yielding the colloidal solutions again.

The solutions are fairly stable, but decompose if shaken with barium sulphate or animal charcoal, the metals coagulating.

In the finely divided condition the metals are likewise possessed of powerful catalytic powers. These are shown to advantage when asbestos soaked in a solution of the chloride of any one of the metals is ignited, whereby the metal is obtained as a deposit on the surface of the asbestos in a high state of subdivision. In such circumstances

1 See Paal and his co-workers, Ber., 1905, 38, 1406, 2414; 1907, 40, 2201, 2209; 1908, 41, 2273, 2283.
they readily oxidise hydrogen and hydrocarbons in the presence of air. They may be arranged in the following order of activity, osmium proving decidedly the most reactive and rhodium the least:

Osmium; palladium; platinum and ruthenium; iridium; rhodium.¹

It is interesting to compare this order with that found for the activity of the colloidal metals in regard to the decomposition of hydrogen peroxide. The change in position of the osmium is remarkable.

In this connection it is interesting to note that minute traces of these metals may be detected on asbestos by holding the latter, immediately after heating to redness in a Bunsen flame, in a mixture of coal gas and air. The particles of metal become incandescent in consequence of their catalytic activity in causing the union of the coal gas and air. By this means it has been found possible² to detect the following traces:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>0-002 mg.</td>
</tr>
<tr>
<td>Iridium</td>
<td>0-005</td>
</tr>
<tr>
<td>Rhodium</td>
<td>0-0009</td>
</tr>
<tr>
<td>Palladium</td>
<td>0-0005</td>
</tr>
</tbody>
</table>

Ruthenium, rhodium, iridium and platinum are characterised by yielding, upon reduction of their salts, highly explosive powders. Osmium and palladium do not appear to share this property.³

**Comparative Study of Iron, Cobalt, and Nickel**

*The Metals.*—In many respects metallic iron, cobalt, and nickel closely resemble one another. The greatest difference between their atomic weights is only three units, and their specific heats are similar, as might be expected from Dulong and Petit’s Law. Again, all three metals become passive or inert when exposed to certain oxidising influences such as anodic polarisation in alkaline solution. This is usually attributed to the formation of a skin of oxide upon the surface of the metal which protects the under layers from attack; but probably no single explanation will suffice for every case. Hydrogen is readily occluded by each of the metals to an extent dependent upon a variety of factors such as temperature, length of exposure to the gas, and the physical condition of the metal.

On the other hand, the metals exhibit an interesting gradation in properties. For example, the melting- and boiling-points gradually fall as we pass from iron to nickel. Whilst it is true that all three metals are magnetic at ordinary temperatures, iron retains this property at very high temperatures, cobalt loses it at about 1150° C., and nickel at 320° C.

Each of the metals is stable in dry air, and neither cobalt nor nickel is greatly affected by moist air, merely becoming tarnished in process of time. Iron, however, readily rusts under such conditions, yielding a reddish brown, pulverulent mass of oxide which tends to stimulate further corrosion. In this respect iron is unique.

In the finely divided condition each of the metals can act as a catalyser, as, for example, in the reduction of unsaturated hydrocarbons. Thus acetylene in the presence of excess of hydrogen on

coming into contact with the metals at temperatures somewhat below 200° C. is reduced to methane, ethane, etc., liquid petroleum being also formed. Nickel acts most vigorously, but cobalt is less active, whilst iron will not act in all reactions.

**Compounds.**—Even a superficial study of the derivatives of iron, cobalt, and nickel shows that a decided gradation in properties occurs as we pass from iron through cobalt to nickel. Thus iron readily forms two classes of salts, namely, ferrous and ferric, in which the metal is respectively divalent and trivalent. Of these the ferric salts are generally speaking the more stable. Nickel, on the other hand, usually functions as a divalent metal, and although evidence appears to have been obtained in favour of the possibility of the momentary existence of salts of trivalent nickel, such salts are unstable in the very highest degree. Cobalt lies between these two extremes, for although its ordinary trivalent derivatives are unstable, double salts in which cobalt has a valency of three are not only well known, but are remarkable for their stability.

By way of illustrating the foregoing it is instructive to study the cyanogen derivatives of the metals. On adding a solution of potassium cyanide in excess to one of a ferrous salt the precipitate first formed readily passes into solution yielding potassium ferrocyanide, \( K_4 Fe(CN)_6 \), in which the iron continues to function as a divalent metal. The aqueous solution contains the complex ion \( Fe(CN)_6^{3-} \), which constitutes the negative radicle. Upon oxidation potassium ferricyanide, \( K_3 Fe(CN)_6 \), is produced, which contains the negative radicle \( Fe(CN)_6^{3-} \) in which the iron is trivalent.

Cobalt behaves in an analogous manner, yielding cobalto- and cobalti-cyanides, although the former are not characterised by great stability. It is otherwise with nickel, however, for salts of this metal on treatment with excess of potassium cyanide solution yield potassium nickelocyanide, \( K_2 Ni(CN)_4 \). The divalent negative ion \( Ni(CN)_4^{2-} \) is present in solutions of this salt, so that the foregoing formula is probably more correct than \( 2KCN . Ni(CN)_2 \). Nevertheless the salt is readily decomposed by addition of oxidising agents, such as sodium hypobromite, yielding a black precipitate of nickel peroxide. Indeed, this difference in behaviour between cobalt and nickel salts is made use of in separating the two metals in qualitative analysis, for nickeli-cyanides are not known.

Carbon readily dissolves in molten iron, yielding the carbide \( Fe_3 C \), known technically as cementite. It is this power of absorbing carbon that renders iron so extremely valuable for metallurgical purposes, since its physical properties are entirely transformed thereby. From a relatively soft metal it may be converted into one exhibiting all grades of hardness up to that which readily enables it to scratch glass. Its other physical properties, such as elasticity, tensile strength, brittleness, etc., are also stupendously influenced by the presence of carbon. Indeed, in this respect, iron is unique amongst the metallic elements.

Carbon dissolves likewise in molten cobalt, and at very high temperatures the carbide \( Co_2 C \) is produced, but the carbide decomposes into cobalt and graphite with such rapidity upon cooling that it cannot be detected even in quenched specimens. The nickel analogue, \( Ni_2 C \), has also been obtained. These substances, however, do not possess a tithe of the interest or importance attaching to their iron analogue.

CHARACTERISTICS OF THE ELEMENTS OF GROUP VIII

All three metals unite with carbon monoxide to form tetracarbonyls of general formula M(CO)₄. Of these the iron derivative yields dark green prismatic crystals which are stable under ordinary conditions but dissociate into metallic iron and carbon monoxide at 140° to 150° C. Cobalt tetracarbonyl likewise occurs in the solid condition at ordinary temperatures, in the form of orange crystals, which, however, decompose on exposure to air, yielding a basic carbonate. The nickel analogue is a liquid, boiling at 43.2° C., and solidifying at — 25° C.

Iron unites with oxygen to form three well-defined oxides, namely, ferrous oxide, FeO; ferroso-ferric oxide, Fe₂O₃; and ferric oxide, Fe₃O₄. These are basic in character as a rule, although ferric oxide also possesses feeble acidic properties, as evidenced by the fact that derivatives of calcium, lead, copper, and other metals have been obtained. The dioxide, FeO₂, has not been isolated, but ferrites have been prepared, such as barium ferrite, BaO.FeO₄ or BaFeO₃, in which the oxide functions as an acid radicle. Similarly attempts to prepare the trioxide, FeO₃, have hitherto proved abortive although barium ferrate, BaFeO₄, is known.

Cobalt likewise yields a monoxide, CoO; cobaltocobaltic oxide, Co₂O₃; and cobaltic oxide, Co₃O₄. The last named is interesting inasmuch as its hydrate, Co(OH)₃, dissolves in hydrochloric acid evolving chlorine, thus behaving like a peroxide. In this respect it closely resembles nickel dioxide, and the resemblance is all the more striking since nickel does not appear to yield a sesquioxide. Cobalt dioxide, CoO₂, has also been prepared; it unites with bases to form cobaltites.

Both nickel monoxide, NiO, and nickello-nickelic oxide, Ni₃O₄, are known, but, as stated above, there is a doubt about nickelic oxide, Ni₂O₃, the substance usually described as such being in all probability the dioxide, NiO₂. Barium nickelite, BaO.2NiO₂, has been prepared.

Ferrous hydroxide, Fe(OH)₂, and cobaltous hydroxide, Co(OH)₂, are characterised by the readiness with which they absorb oxygen from the air, yielding brown oxidised products. Nickelous hydroxide, Ni(OH)₂, on the other hand, is oxidised considerably less readily.

Cobalt sesquisulphide, Co₃S₄, results when a mixture of sulphur and the carbonates of cobalt and potassium are raised to white heat. Nickel in similar circumstances yields K₄S₃NiS, and thus resembles palladium and platinum, whereas cobalt behaves more like rhodium and iridium. The position of nickel after cobalt in the Periodic Table is thus supported.

The sulphates of divalent iron, cobalt, and nickel all occur in various stages of hydration. The heptahydrates are isomorphous. With sulphates of the alkali metals isomorphous double salts are formed containing six molecules of water, and having the general formula M₂SO₄.RSO₄.6H₂O. Ferrie sulphate and cobaltic sulphate are known, but not nickelic sulphate.

Both iron and cobalt, when trivalent, yield stable double sulphates with ammonium and the alkali metals, containing twenty-four molecules of water. These are known as alums, and to them the general formula M₂SO₄.R₃(SO₄)₃.24H₂O may be ascribed. They usually crystallise in well-defined octahedra. Nickel, on the contrary, does not yield salts of this type, since nickelic sulphate cannot exist.

The chlorides of iron, cobalt, and nickel are of peculiar interest. Ferrous chloride, when perfectly pure and free from water, is a white,
scaly, crystalline substance, volatile at yellow heat in the absence of air. It readily absorbs ammonia, yielding a voluminous white mass, two definite ammoniates, namely, the diammoniate, FeCl₂.2NH₃, and the hexammoniate, FeCl₂.6NH₃, having been isolated. The hydrated salt contains four molecules of water and yields bluish, monoclinic crystals. Solutions of ferrous chloride in various solvents readily absorb nitric oxide. Cobaltous chloride is, in many of its properties, entirely different from the preceding salt. When anhydrous it occurs as blue crystalline scales. Numerous hydrates are known, of which the hexahydrate is the most common, occurring as dark red monoclinic prisms. In the cold, a saturated solution of cobalt chloride is rose-coloured, but on warming it becomes violet between 25° C. and 50° C., and above the latter temperature it assumes a blue colour. This is entirely characteristic of the cobalt salt, neither ferrous nor nickelous chloride exhibiting this phenomenon. Cobaltous chloride yields a hexammoniate, CoCl₂.6NH₃, in the form of dark rose-red octahedral crystals when ammonia is passed into a concentrated aqueous solution of cobaltous chloride in the entire absence of air. Nickelous chloride, when anhydrous, occurs as golden scales which readily dissolve in water, yielding on crystallisation green monoclinic prisms of the hexahydrate, NiCl₂.6H₂O, isomorphous with the corresponding cobalt salt. Like ferrous chloride, anhydrous nickelous chloride swells to a white powder in the presence of ammonia, the hexammoniate, NiCl₂.6NH₃, being produced.

Ferric chloride is a well-known, stable salt; cobaltic chloride has not been isolated although indications of its possible existence have been obtained; nickel does not yield a trivalent halide.

For the sake of easy comparison and contrast a few of the more important compounds of iron, cobalt, and nickel are indicated in the accompanying table:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃C</td>
<td>Co₃C</td>
<td>Ni₃C</td>
</tr>
<tr>
<td>Fe(CO)₄ (solid)</td>
<td>Co(CO)₄ (solid)</td>
<td>Ni(CO)₄ (liquid)</td>
</tr>
<tr>
<td>K₄Fe(CN)₆</td>
<td>K₄Co(CN)₆</td>
<td>K₂Ni(CN)₁</td>
</tr>
<tr>
<td>K₃Fe(CN)₆</td>
<td>K₃Co(CN)₆</td>
<td>NiO</td>
</tr>
<tr>
<td>FeO</td>
<td>CoO</td>
<td>Ni₃O₂</td>
</tr>
<tr>
<td>Fe₂O₄</td>
<td>Co₂O₂</td>
<td>NiO₂</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Co₂O₃</td>
<td>NiSO₄·7H₂O</td>
</tr>
<tr>
<td>(FeO₂)</td>
<td>Co₂O₂</td>
<td>M₂SO₄·NiSO₄·6H₂O</td>
</tr>
<tr>
<td>FeSO₄·7H₂O</td>
<td>CoSO₄·7H₂O</td>
<td>M₂SO₄·NiSO₄·6H₂O</td>
</tr>
<tr>
<td>M₂SO₄·FeSO₄·6H₂O</td>
<td>M₂SO₄·CoSO₄·6H₂O</td>
<td>M₂SO₄·NiSO₄·6H₂O</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃·9H₂O</td>
<td>Co₉(SO₄)₃·18H₂O</td>
<td>Ni₄N₂</td>
</tr>
<tr>
<td>M₂SO₄·Fe₂(SO₄)₃·24H₂O</td>
<td>M₂SO₄·Co₂(SO₄)₃·24H₂O</td>
<td>NiCl₂</td>
</tr>
<tr>
<td>Fe₄N₂</td>
<td>Co₄N₂</td>
<td>-</td>
</tr>
<tr>
<td>FeCl₂</td>
<td>CoCl₂</td>
<td>-</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>(? CoCl₃)</td>
<td>-</td>
</tr>
</tbody>
</table>
Characteristics of the Elements of Group VIII

Position in the Periodic Table.—In many respects iron, cobalt, and nickel constitute interesting intermediaries between manganese and copper. So close indeed is the connection between manganese, iron, and cobalt, that manganese has frequently been taken out of Group VII and placed in Group VIII along with iron, thus converting the first triadic group into a tetradic one. As illustrating the gradation in properties on passing from manganese to nickel, it may be observed that manganese, iron, and nickel yield carbides of the type \( M_2C \), the heats of formation being as follows:

\[
\begin{align*}
\text{Mn}_2C & \quad 12.9 \text{ calories} \\
\text{Fe}_2C & \quad 15.3 \text{ "} \\
\text{Ni}_2C & \quad 39.4 \text{ "}
\end{align*}
\]

The first named is stable, the second is slightly unstable, whilst nickel carbide is characterised by great instability.

Moissan in 1880 called attention to the fact that the affinities of chromium, manganese, iron, cobalt, and nickel for oxygen and the heats of formation of oxides, chlorides, bromides, iodides, and sulphides decrease as the atomic weights rise.

When a caustic alkali is added to a solution of a ferrous salt, white ferrous hydroxide is precipitated. This readily oxidises in air, yielding brown, ferric hydroxide. A manganous salt behaves in a precisely similar manner. It is instructive to note, however, that when ammonium hydroxide solution is added to one of a manganous salt in the presence of ammonium chloride, the hydroxide is not precipitated, and under similar conditions ferrous hydroxide is only partially thrown out from a solution of a ferrous salt.

Although the dioxide \( \text{FeO}_2 \) has not been isolated with certainty, derivatives such as strontium ferric, \( \text{SrO}_2 \), and barium ferrite, \( \text{BaO}_2 \), are known, corresponding to the manganites. Ferrates, corresponding in composition to the manganates, have also been obtained, the most stable of which is the barium salt, \( \text{BaFeO}_4 \).

Both iron and manganese yield divalent and trivalent series of salts as exemplified by their chlorides, \( \text{FeCl}_2 \), \( \text{MnCl}_2 \); \( \text{FeCl}_3 \), \( \text{MnCl}_3 \), and sulphates, \( \text{FeSO}_4 \), \( \text{MnSO}_4 \); \( \text{Fe}_2(\text{SO}_4)_3 \), \( \text{Mn}_2(\text{SO}_4)_3 \). Further, manganous chloride and bromide, together with their hydrates, are isomorphous with the corresponding ferrous, cobalt, and nickel salts. Ferrous sulphate is interesting, for it exists in several stages of hydration, the heptahydrate, \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \), and tetrahydrate, \( \text{FeSO}_4 \cdot 4\text{H}_2\text{O} \), being isomorphous with the corresponding manganese salts, \( \text{MnSO}_4 \cdot 7\text{H}_2\text{O} \) and \( \text{MnSO}_4 \cdot 4\text{H}_2\text{O} \). The pentahydrate, \( \text{FeSO}_4 \cdot 5\text{H}_2\text{O} \), is isomorphous with copper sulphate, \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \), and mixed crystals of the two salts are readily obtainable.

Manganic, ferric, and cobaltic sulphates yield with the sulphates of the alkali metals well-defined isomorphous octahedral crystalline compounds known as alums. These have the general formulæ

\[
\begin{align*}
\text{M}_2\text{SO}_4 \cdot \text{Mn}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} & \quad \text{M}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}, \\
\text{and} & \quad \text{M}_2\text{SO}_4 \cdot \text{Co}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}.
\end{align*}
\]

1 The main arguments in favour of this have recently been summarised by Bichowsky,


2 Ruff and Geist, Ber., 1913, 46, 400.


4 Moesz and Borok, Ber., 1909, 42, 4279.

5 Rosell, J. Amer. Chem. Soc., 1895, 17, 760; Baschieri, Gazzetta, 1906, 36, [ii], 282.
The sulphides of divalent manganese, iron, cobalt, and nickel are all precipitated in neutral solution by addition of ammonium sulphide; all are insoluble in water, but soluble in mineral acids.

The carbonates, MnCO₃, FeCO₃, CoCO₃, and NiCO₃, are known, and the natural carbonates of manganese and iron occur in very intimate association.

Nickel, on the other hand, bears a close similarity to copper. It does not, like copper, yield well-defined monovalent salts, but the divalent salts of the two metals are similar. Both have a bluish or greenish colour, which is enhanced by the addition of ammonia owing to the formation of complex ammoniates. Pickering has drawn attention to the fact that the colour intensity of organic salts of nickel decreases with dilution in a similar manner to that of copper derivatives. The organic salts dissolve in caustic alkali to form compounds resembling those yielded by copper. In some cases jellies are produced, as with copper. For example, potassium nickelo-citrate yields, with potassium hydroxide, a permanent dark green jelly.

**Comparative Study of Iron, Ruthenium, and Osmium**

The principal characteristics of these metals are shown in the table on page 5. It will be observed that their densities rise steadily with increased atomic weight, osmium in certain circumstances having a greater density, namely, 24, than any other known substance.

All three metals yield dichlorides and trichlorides and, in the case of ruthenium and osmium, series of complex salts are known under the names of rutheno-chlorides or chlor-ruthenites, M₂RuCl₅, and osmo-chlorides or chlor-osmites, M₃OsCl₈ or MCl₃·M₂OsCl₅.

Ruthenium and osmium also yield series of more highly chlorinated salts known respectively as chlor-ruthenates, M₂RuCl₆, and chlor-osmates, M₃OsCl₉. These are isomorphous. Iron does not yield corresponding derivatives. It is interesting to note, however, that ruthenium and osmium resemble iron in forming nitroso derivatives. For example, FeCl₃·NO, RuCl₃·NO·H₂O, and osmianic acid, OsNO·O·OH, are now well known.

Considerable resemblance may be traced between the oxides of iron, ruthenium, and osmium. Although it is true that ruthenium monoxide has not as yet with certainty been prepared whilst osmium monoxide is believed to exist and ferrous oxide is exceedingly well defined, yet all three metals yield a sesquioxide of the type M₂O₃.

Iron dioxide is not known in the free state, but it can exist in combination, as witness such ferrites as barium ferrite, BaFeO₃. The dioxides of ruthenium, RuO₂, and osmium, OsO₂, are known. The former is isomorphous with cassiterite, SnO₂, and rutile, TiO₂; and combines with bases to form ruthenites, for example, barium ruthcnite, BaRuO₃.

Osmium dioxide is characterised by its remarkable power of forming what are commonly known as osmyl derivatives of general formula M₄(OsO₂)ₓ. Iron trioxide can only exist in combination with bases, as, for example, in barium ferrate, BaFeO₄. Ruthenium does not yield a separate trioxide either, although its derivatives are better known than

---

the corresponding iron ones. The best known of these is potassium ruthenate, $K_2\text{RuO}_4\cdot H_2O$. Osmium yields a hydrated trioxide, known as osmic acid, $\text{Os}_2\text{O}_7\cdot H_2O$ or $\text{H}_2\text{OsO}_4$, the most important salt of which is potassium osmate, $K_2\text{OsO}_4\cdot 2H_2O$.

Potassium per-ruthenate, $KRuO_4$, is analogous to, but not isomorphous with, potassium permanganate.

An interesting series of osmyl oxy-derivatives is known, containing the radicle $\text{OsO}_3$, and to which the general formula $M_2(\text{OsO}_3)X_2$ is given.

Ruthenium and osmium are unique in yielding tetroxides, $\text{RuO}_4$ and $\text{OsO}_4$ respectively; the former, a golden yellow mass, melting at 25-5° C., and the latter a white crystalline substance of an exceedingly poisonous nature. Both oxides are readily volatilised. Although these oxides are soluble in water they do not yield hydroxides, and seem incapable of acting like acidic oxides. This is remarkable in view of the acidic tendencies of the higher oxides of most metals.

Iron combines with carbon monoxide to form three carbonyls, namely, $\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$. Ruthenium yields a dicarbonyl, $\text{Ru}(\text{CO})_2$, when exposed at 300° C. to carbon monoxide under a pressure of 400 atmospheres. It thus resembles molybdenum, which forms $\text{Mo}(\text{CO})_6$, and which is situated in the same horizontal series in the Periodic Table.

Iron, ruthenium, and osmium yield complex cyanides in which the metal enters the negative radicle. These are known respectively as ferro-cyanides, $M_4\text{Fe}(\text{CN})_6$, rutheno-cyanides, $M_4\text{Ru}(\text{CN})_6$, and osmo-cyanides, $M_4\text{Os}(\text{CN})_6$. Their salts exhibit close similarity, and are isomorphous. In addition to ferrocyanides, iron yields a series of salts known as ferricyanides of general formula $M_3\text{Fe}(\text{CN})_6$, and nitroso salts termed nitro-prussides, $M_2\text{Fe}(\text{CN})_5\text{NO}$. This property is not shared by ruthenium and osmium. In order to facilitate the comparison of the compounds of the three metals under discussion, their more important derivatives are given in the following table:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{FeCl}_2$</td>
<td>$\text{RuCl}_2$</td>
<td>$\text{OsCl}_2$</td>
</tr>
<tr>
<td>$\text{FeCl}_2\cdot \text{NO}$</td>
<td>$\text{RuCl}_3\cdot \text{NO} \cdot 5\text{H}_2\text{O}$</td>
<td>$\text{OsCl}_3$</td>
</tr>
<tr>
<td>$\text{FeCl}_3$</td>
<td>$\text{RuCl}_3$</td>
<td>$\text{OsCl}_3$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>$\text{M}_2\text{RuCl}_5$</td>
<td>$\text{M}_2\text{OsCl}_5$</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3\cdot \text{(FeO}_2\text{)}$</td>
<td>$\text{M}_2\text{RuCl}_6$</td>
<td>$\text{M}_2\text{OsCl}_6$</td>
</tr>
<tr>
<td>$\text{BaFeO}_3$</td>
<td>$\text{BaRuO}_3$</td>
<td>$\text{OsO}_2$</td>
</tr>
<tr>
<td>$\text{BaFeO}_4$</td>
<td>$\text{K}_2\text{RuO}_4\cdot \text{H}_2\text{O}$</td>
<td>$\text{K}_2\text{OsO}_4\cdot 2\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{K}_4\text{Fe(CN)}_6\cdot 3\text{H}_2\text{O}$</td>
<td>$\text{K}_4\text{Ru(CN)}_6\cdot 3\text{H}_2\text{O}$</td>
<td>$\text{K}_4\text{Os(CN)}_6\cdot 3\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>

1 Unfortunately the tetroxide, $\text{OsO}_4$, is usually mis-termed "osmic acid."
Comparative Study of Cobalt, Rhodium, and Iridium

The principal characteristics of these metals are shown in the table on page 5. It will be observed that their specific heats fall with rise of atomic weight, as is to be expected from Dulong and Petit's Law. Their densities increase with their atomic weights.

In many ways metallic cobalt resembles iron and nickel in its physical properties. Iridium has frequently been compared to gold in virtue of its resistance to acids and general corroding media, but in its colour and general physical properties its resemblance to gold is not so marked; in fact it is much more like platinum.

The more important simple derivatives of cobalt are divalent, the metal only yielding stable trivalent salts in conjunction with other metallic derivatives, as, for example, the cobalti-nitrites and cobalti-cyanides, or in the complex ammino derivatives. Rhodium and iridium function almost exclusively as trivalent metals in their salts.

Cobalt yields a well-defined dichloride, CoCl₂, but its trichloride has not as yet been isolated, although indications of its possible existence are not entirely wanting. The existence of rhodium dichloride, on the other hand, is uncertain, but the trichloride, RhCl₃, is well known. It occurs in two varieties, one of which is anhydrous and insoluble in water and acids, whilst the other form is hydrated and soluble. (Compare chromium.)

Similarly iridium dichloride appears to be incapable of a separate existence, although it occurs in combination with certain other stable salts, as, for example, IrCl₃.K₂SO₃.2NH₄Cl.4H₂O.

Iridium, like rhodium, also forms a trichloride, IrCl₃.

Although cobalt chloride can unite with other chlorides to form double salts, no well-defined series of such salts exists. Rhodium and iridium trichlorides yield hexachlor-rhodites and hexachlor-iridites respectively, of general formulae M₂RhCl₆ and M₃IrCl₄. These are isomorphous, and are analogous in constitution to the hexachlor-osmites, M₃OsCl₆.

Rhodium is unique in forming a second series of salts, namely, the pentachlor-rhodites, of general formula M₂RhCl₅, in which respect it resembles ruthenium.

On the other hand, iridium yields a tetrachloride, IrCl₄, and this, with chlorides of the alkali metals, produces a series of salts known as hexachlor-iridates, of general formula M₂IrCl₆, isomorphous with the analogous derivatives of osmium, ruthenium, palladium, and platinum. These form an interesting link between these metals.

Cobalt monoxide is a well-defined chemical entity, but the existence of monoxides of rhodium and iridium has not as yet been satisfactorily demonstrated. All three metals yield sesquioxides, of the type R₂O₃, and dioxides, of the type RO₂. The last named exhibit weak acidic tendencies in that they can unite with bases to form cobaltites, rhodites, and iridites respectively, analogous to the ferrites, ruthenites, and osmites mentioned in the previous section, and exhibiting an interesting relationship to the chromites and manganites.

Cobalt, rhodium, and iridium yield sulphates of the type R₂(SO₄)₂, and these combine with sulphates of the alkali metals to produce alums, of the general formula M₂SO₄.R₂(SO₄)₂.24H₂O. These are well-defined
crystalline salts, isomorphous with the better known iron, manganese, and aluminium alums.

Cobalt and rhodium yield complex molybdates which are chemically and crystallographically analogous to the corresponding complex molybdates of aluminium, iron, and chromium.¹

Cobalt yields an interesting series of double nitrites, the most important member of which is Fischer's salt or potassium cobaltinitrite, $K_3Co(NO_2)_6 \cdot 2H_2O$. Rhodium shares this property to a considerable extent, and the potassium salt, $K_3Rh(NO_2)_6$, may be used in an analogous manner to Fischer's salt, namely, in the preparation of pure rhodium, and also for the quantitative estimation of that metal.

Iridium, too, yields double nitrites, the potassium salt, $K_3Ir(NO_2)_6$, in particular having been isolated. It is conceded, however, that the double nitrites of iridium are less important than those of the two preceding metals.

Cobalt, like iron, yields complex cyanide derivatives known respectively as cobalto-cyanides, $M_4Co(CN)_6$, and cobalti-cyanides, $M_3Co(CN)_6$. Of these, the latter alone are important. Rhodium and iridium in a similar manner yield rhodi-cyanides, $M_3Rh(CN)_6$, and iridi-cyanides, $M_3Ir(CN)_6$.

Cobalt, rhodium, and iridium are also characterised by their power of yielding complex ammino derivatives, and in this manner resemble palladium and platinum. These derivatives are a remarkable series of substances entirely distinct in most of their properties from the more usual inorganic salts of the metals in question, and are dealt with separately in Volume X of this Series.

In order to assist in the direct comparison of the chief derivatives of cobalt, rhodium, and iridium, the following table has been compiled:

<table>
<thead>
<tr>
<th>Cobalt</th>
<th>Rhodium</th>
<th>Iridium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CoCl_2$</td>
<td>$RhCl_3$</td>
<td>$IrCl_3$</td>
</tr>
<tr>
<td>$(CoCl_3)_3$</td>
<td>$IrCl_4$</td>
<td>$M_3IrCl_6$</td>
</tr>
<tr>
<td>$M_2Co(NO_2)_6 \cdot 2H_2O$</td>
<td>$M_2Rh(NO_2)_6 \cdot 2H_2O$</td>
<td>$M_3Ir(NO_2)_6$</td>
</tr>
<tr>
<td>$M_3Co(CN)_6$</td>
<td>$M_3Rh(CN)_6$</td>
<td>$M_3Ir(CN)_6$</td>
</tr>
</tbody>
</table>

¹ See Barbieri, Atti R. Accad. Lincei, 1914, [v], 23, i, 334.
Comparative Study of Nickel, Palladium, and Platinum

Examination of the table on page 5, which gives the principal physical data concerning these metals, reveals the fact that the densities rise but the specific heats fall with increasing atomic weight. This latter observation is quite in accord with Dr. Long and Petit’s Law.

Metallic nickel closely resembles cobalt both in its physical and its chemical properties, and platinum exhibits many analogies to iridium, whilst rhodium also exhibits certain analogies to palladium. For example, the two last-named metals are both converted into sulphates on fusion with potassium hydrogen sulphate, whereas neither platinum nor iridium is affected by this treatment. On the other hand, palladium appears to stand apart somewhat in certain respects. Thus, it is unique in displacing mercury from its cyanide. Just as nickel resembles copper in many respects, so can an analogy be traced between palladium and silver, which latter is its adjoining element in the second long horizontal period in the Periodic Table. For example, on solidifying from the molten condition in an oxidising atmosphere palladium “spits” just like silver, yielding a hollow ingot. Platinum similarly resembles gold in many of its properties, to wit, its resistance to acid attack; its solubility in aqua regia; and its ready reduction from its salts.

Palladium is characterised by a remarkable power of absorbing or occluding hydrogen. The actual volume of gas absorbed depends not merely upon the temperature, but upon the physical condition of the metal, and at ordinary temperatures ranges from about 375 to 850 volumes per unit volume of compact palladium. Nickel and platinum share this property, but to a very much smaller extent.

Nickel behaves as a divalent element, and its dichloride, NiCl₂, is a well-defined salt, no higher chloride being known. Palladium is similar, but its dichloride, PdCl₂, yields a series of double salts with the chlorides of the alkali metals. These have the general formula M₂PdCl₄, and are known as tetrachlor-palladites. Platinum resembles palladium in this respect, platinum dichloride, PtCl₂, and chlor-platinites of the type M₂PtCl₄, being well known. Potassium chlor-palladite is isomorphous with potassium chlor-platinitite.

Palladium does not form stable higher chlorides, although the trichloride has been obtained in solution and the tetrachloride can exist in combination, giving rise to a series of salts, namely, hexachlor-palladates, M₆PdCl₂₆. These are analogous to, isomorphous with, but not as stable as, the hexachlor-platinates, M₆PtCl₂₆, which are better known, and which are derived from platinic chloride, PtCl₄, a well-defined and stable salt. Similarly pentachlor-palladites, M₆PdCl₃₅, and pentachlor-platinites, M₆PtCl₃₅, are known. The trichloride of platinum, PtCl₃, has also been isolated. The fact, however, that pentachlor-palladites and hexachlor-palladates can exist at all, whilst nickel yields no such compounds, affords an interesting link between palladium and platinum, and further justifies the intermediate position of palladium between nickel and platinum in the triad under discussion.

It is interesting to compare these chlor-palladates and chlor-platinitates with the corresponding derivatives of iridium and osmium,
with which they are isomorphous. And it is worthy of note that the chlor-platinates are isomorphous\(^1\) with the chlor-stannates, \(M_2SnCl_6\).

Electrolysis of platinic chloride solution shows that the platinum is present in the complex anion, and not in the cation, as would be expected. In this respect the metal resembles gold,\(^2\) since electrolysis of \(AuCl_3.\text{H}_2\text{O}\) yields to similar conclusions.

Nickel, palladium, and platinum yield monoxides and dioxides; the dioxides of nickel and platinum exhibit feebly acidic tendencies as manifested by the existence of such compounds as barium nickelite, \(\text{BaO}.2\text{NiO}_3\), and potassium platinate, \(K_2\text{PtO}_3.3\text{H}_2\text{O}\) or \(K_2\text{Pt(OH)}_3\). This latter substance is isomorphous with potassium stannate, \(K_2\text{SnO}_3.3\text{H}_2\text{O}\), and thus affords another interesting link between platinum and tin.

Nickel nitrite can unite with the nitrites of certain other metals to yield triple salts resembling in appearance, though not in constitution, the cobaltii nitrites. The triple salt, \(2\text{KNO}_2.\text{Ca(NO}_2)_2.2\text{Ni(NO}_2)_2\), is a case in point, being insoluble in water and having a yellow colour closely similar to that of Fischer's salt.

Both palladium and platinum, particularly the latter, yield regular series of complex nitrites in which the metal enters the negative radicle. These are known respectively as pallado-nitrites, \(M_2\text{Pd(NO}_2)_4\), and platino-nitrites, \(M_2\text{Pt(NO}_2)_4\).

Nickel yields a tetracarbonyl when, in a finely divided condition, it is warmed in a current of carbon monoxide. Both palladium black and platinum black absorb carbon monoxide, yielding what appears to be a compound, although attempts to isolate the substance have not as yet proved successful. On heating to 250\(^\circ\) C. the substances decompose, evolving carbon monoxide.

Nickel cyanide combines with potassium cyanide to form potassium

---

\(\begin{array}{|c|c|c|}
\hline
\text{Nickel.} & \text{Palladium.} & \text{Platinum.} \\
\hline
\text{NiCl}_2; & \text{PdCl}_2; & \text{PtCl}_2; \\
\text{---} & \text{M}_2\text{PdCl}_4 & \text{M}_2\text{PtCl}_4 \\
\text{---} & \text{PdCl}_3.\text{CO} & \text{PtCl}_3.\text{CO} \\
\text{NiO; NiSO}_4 & \text{PdCl}_3;M_2\text{PdCl}_5 & \text{PtCl}_3;M_2\text{PtCl}_5 \\
\text{Ni}_2\text{O}_4 & \text{---} & \text{PtCl}_4;M_2\text{PtCl}_6 \\
\text{NiO}_2; & \text{PdO}_2; & \text{PtCl}_6; \\
\text{---} & \text{---} & \text{PtO} \\
\text{Ni(NO}_2)_2;M_4\text{Ni(NO}_2)_6 & \text{---} & \text{Pt}_3\text{O}_4 \\
\text{Ni}_2\text{C; Ni(CO)}_4 & \text{---} & \text{Pt}_3\text{O}_5 \\
\text{Ni(CN)}_2;M_4\text{Ni(CN)}_4 & \text{Pd(CN)}_2;M_2\text{Pd(CN)}_4 & \text{Pt(CN)}_2;M_2\text{Pt(CN)}_4 \\
\text{Ammoniates} & \text{Ammoniates} & \text{Ammoniates} \\
\hline
\end{array}\)

---

\(^1\) This analogy has been studied by Bellucci and Parravano, \(\text{Atti R. Accad. Lincei}, 1904, [v], 13, ii, 307.\)

\(^2\) Hittorf and Salkowski, \(\text{Zeitsch. physikal. Chem.}, 1899, 28, 546.\)
nickel-cyanide, $K_2Ni(CN)_4$. Although in solution the ion $Ni(CN)_4^{2-}$ is present, the compound is unstable, being readily decomposed by oxidising agents such as sodium hypobromite, with deposition of a black hydrated oxide of nickel.

Palladium and platinum likewise yield pallado-cyanides, $M_2Pd(CN)_4$, and platino-cyanides, $M_2Pt(CN)_4$, which are isomorphous.

Nickel salts readily combine with ammonia to form ammoniates, as, for example, the hexammoniates of nickel chloride, $NiCl_2\cdot6NH_3$, and sulphate, $NiSO_4\cdot6NH_3$. Palladium salts act similarly.

Platinum salts yield complex ammino derivatives resembling those of cobalt. These are entirely distinct from the more usual inorganic salts of these metals, and are dealt with in Volume X of this Series.

For the sake of easy comparison, a few of the more important compounds of nickel, palladium, and platinum are given in the table on page 17.
CHAPTER II

COBALT AND ITS COMPOUNDS

COBALT

Symbol, Co. Atomic weight, 58.97 (O = 16)

Occurrence.—Cobalt very seldom occurs free in nature. It is found alloyed with iron in meteorites, but only in small quantity. The ores of cobalt are not widely distributed like those of iron, and this is a serious handicap in the commercial development of the metal. The more important ores are as follow: cobaltite, cobalt glance, or bright white cobalt, CoAsS, found in Sweden. It crystallises in cubes, octahedra, and pyritohedra; hardness 5.5; density 6.2. It is silver-white in colour and has a metallic lustre. Glaucodote has a similar chemical composition, but contains iron as well. Formula, (FeCo)AsS; crystal form, orthorhombic. Smaltite, CoAs₂, occurs in Saxony and Bohemia, and crystallises in cubes and cubo-octahedra; hardness 5.5; density 6.2. It forms isomorphous mixtures with the corresponding arsenide of nickel, NiAs₂, known as chloanthite, different specimens containing varying amounts of the two metals, as well as, not infrequently, iron and sulphur. Another diarsenide of cobalt occurs in nature as the mineral safflorite, CoAs₂, and contains iron. It crystallises in the orthorhombic system. Skutterudite, a Norwegian mineral crystallising in octahedra, is the triarsenide, CoAs₃.

A fairly common mineral is the ortho-arsenate, Co₃(AsO₄)₂·8H₂O, known as erythrite, or cobalt bloom. It is crimson in colour and isomorphous with vivianite (ferrous phosphate). Other minerals are asbolan, earthy cobalt, or wad, (CoMn)O·2MnO₂·4H₂O; and linarite, (CoNiFe)₃S₄. The former contains anything from 2 to 20 per cent. of cobalt, and is found in New Caledonia and in Spain. Bismuto-smaltite, Co(AsBi)₃. Carrollite, Co₂CuS₄. Willyamite, NiCoSb₂S₂. Jaiipurite, CoS.

Cobalt District, Ontario, Canada, contains the most important ores of cobalt in the form of arsenides, associated with nickel and silver, the last-named metal rendering the ores very valuable. Their cobalt content ranges from 9 to 18 per cent.

The presence of cobalt in the sun’s photosphere has been determined spectroscopically.¹

For the sake of convenient reference, the foregoing minerals are given in the table on page 20, together with their more important physical constants.

History.—The word cobalt is the same as the German Kobold, and Greek κόβαλος, a gnome or malicious sprite, and is akin to the word goblin. Kobold was applied to a mineral associated with silver ores in Saxony, the name being given by the miners because they regarded the ore as poisonous (Skeat). Up to 1540 the mineral was regarded as useless, but Scheurer found that it would colour glass, and that

¹ Lockyer, Compt. rend., 1878, 86, 317.
--- | --- | --- | --- | --- | ---
Absolam or asbolite | See Wad CoSO₄·7H₂O | Flesh-colour | 1.9 | — | —
Bieberite or cobalt vitrile | Co₃(AsBi)₃ | — | — | — | —
Bismuto-cobaltite | Co₂CuS₄ | Steel-grey | 4.85 | 5.5 | Cubic
Cobalt bloom | See Erythrite | — | — | — | —
Cobalt glance | See Cobaltite | — | — | — | —
Cobaltite | CoAsS | Silver-white | 6.2 | 5.5 | Cubic
Earthly cobalt | See Wad Co₃(AsO₄)₂·8H₂O | Crimson | 2.95 | 1.5-2.5 | Monoclinic
Erythrite or erythrine | (FeCo)AsS | Tin-white | 5.95 | 5 | Rhombic
Glaucodote | CoS | Grey | 5.45 | — | —
Japuirite or Sycoporite | (CoNiFe)₃S₄ | — | 5.5 | 4.8-5 | Cubic
Linnaeite | Co₃(AsO₄)₂ | Tin-white | 6-9-7.3 | 4.5-5 | Cubic
Safflorite | CoAs₂ | — | 6.7 | 6 | Cubic
Skutterudite | CoAs₂ | — | 6.7 | 6 | Cubic
Smalitite | Co₃(AsO₄)₂ | — | 6.2 | 5.5 | Cubic
Wad | (CoMn)O.2MnO₂·4H₂O | Black or blue-black | 0.5-6 | 3.4-3 | Amorphous

It gave it a commercial value. In 1733 Brandt first prepared a specimen of impure metallic cobalt, its identity being confirmed by Bergmann in 1790, and again by Tassaert in 1799. The real study of the chemistry of cobalt compounds dates back to the researches of Thénard (1802) and of Proust (1806).

**Preparation of Cobalt.**—The metallurgy of cobalt is complicated by the fact that cobalt ores invariably contain a certain amount of nickel. Since these two metals closely resemble one another in their chemical properties it will be evident that their complete separation on a commercial scale is a matter of considerable difficulty. It is not usually required, however. The details of the actual methods employed in the commercial production of cobalt are kept fairly secret, more particularly as regards the initial stages of the preparation of the crude oxide. We shall, therefore, content ourselves by giving in outline accounts of a few different methods that may be employed. It is convenient to discuss the subject in three sections, namely:

I. Preparation of cobalt oxide from cobalt ores.

II. Purification of cobalt oxide.

III. Preparation of metallic cobalt from its oxide.

I. *Preparation of Cobalt Oxide from Cobalt Ores*

(a) *Arсенical Ores.*—Wöhler's method consists in fusing the finely divided arsenical ores such as smaltite, skutterudite, and cobaltite with three parts by weight of potassium carbonate and three of sulphur. An impure cobalt sulphide results, together with a sulpho-arsenate of potassium, which latter is readily extracted with water. The insoluble residue is again treated in the same manner, and the resulting cobalt

2 Proust, ibid., 1806, [i], 60, 260.
sulphide, after extraction with water, is free from arsenic, but it still contains nickel, iron, lead, copper, and bismuth in the form of sulphides. Prolonged roasting in air or treatment with nitric acid converts all the metals into their sulphates, in which condition they are dissolved in water. Passage of hydrogen sulphide through the acidulated solution precipitates the lead, copper, and bismuth as insoluble sulphides, and the solution containing iron, nickel, and cobalt is filtered off. Addition of nitric acid and calcium carbonate at the boiling-point effects the oxidation and precipitation of the iron in a basic condition, leaving the sulphates of cobalt and nickel in solution.

Liebig's procedure consists in heating the finely divided ore to redness with potassium hydrogen sulphate until fumes cease to be evolved. On cooling, the mass contains a soluble double sulphate of cobalt and potassium, which can be extracted with water, leaving a residue containing insoluble compounds, mainly oxides and arsenic derivatives of iron, nickel, and some cobalt.

It is doubtful if these methods have ever been employed for manufacturing purposes. European arsenical cobalt ores have been worked for cobalt oxide by a process similar to that described later (see p. 86) for working up arsenical nickel ores. Moreover, a certain amount of cobalt oxide is also derived from the arsenical nickel ores, since these usually contain appreciable quantities of cobalt.

The European arsenical ores have now been largely displaced by those from Cobalt District, Ontario, which have been worked for some years by the Canadian Copper Company, who have employed the following process:

The ore is crushed and ground in ball mills to pass through a 30-mesh sieve. It is mixed with suitable fluxes (limestone and quartz) and smelted in small blast-furnaces having a capacity of 25 to 30 tons per twenty-four hours. The products obtained are (i) flue dust, which is returned to the furnaces, and crude arsenious oxide, which is re-sublimed and sold; (ii) a silicate slag, which is thrown away unless it contains more than 10 ounces of silver per ton; (iii) crude silver bullion, which is mechanically detached and cupelled to a fineness of 994 before it is sold to silver refiners; and (iv) a speiss of cobalt, nickel, iron, and copper arsenides, containing considerable amounts of silver. The crude silver bullion contains about three-fourths of the silver present in the ore.

The speiss is crushed and ground with 20 per cent. of sodium chloride till it passes a 30-mesh sieve, and then roasted in reverberatory furnaces. The chloridised product is extracted with water to remove unchanged salt and soluble compounds of cobalt, nickel, and copper. The copper is removed from the liquor by treatment with scrap-iron, and the cobalt and nickel are then precipitated with caustic soda, and the precipitate washed, dried, calcined, and ground. It contains about 40 per cent. of cobalt to 3 per cent. of nickel, since the latter is not attacked so readily as the former in chloridising the speiss; the mixed oxides also contain about 15 ounces of silver per ton.

1 See Wöhler, Pogg. Annalen, 1826, 6, 227; Duflos, Schweigge's J., 1830, 60, 355.
2 Liebig, Pogg. Annalen, 1830, 18, 164.
3 Other methods have been suggested, chief among which are those of Trommsdorff, Ann. Chim. Phys., 1798, 26, 99; 1805, 54, 327; Quesneville, J. Pharm. Chem., 1829, 15, 291, 411; Lonyet, J. prakt. Chem., 1849, 46, 244; Patéria, ibid., 1856, 67, 21; De Witt, ibid., 1857, 71, 239.
The residue from the chloridised speiss, after extraction of soluble cobalt and nickel salts, is extracted with sodium thiosulphate, to dissolve out silver chloride, which is recovered as the sulphide and reduced to metal. The residue is dried, ground, and smelted with quartz to remove most of the iron as a slag. This slag is reworked with more ore in the blast-furnaces, as it contains silver and cobalt. The new speiss simultaneously produced is treated as described above for recovering cobalt and nickel, copper, and silver. The final residue is dried, mixed with 20 per cent. of sodium nitrate and 10 per cent. of sodium carbonate, and roasted in reverberatory furnace to convert the arsenic into sodium arsenate, which is extracted with hot water. The dried residue has the following average composition:

<table>
<thead>
<tr>
<th>Metal</th>
<th>% of Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>30.7</td>
</tr>
<tr>
<td>Nickel</td>
<td>28.5</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1.1</td>
</tr>
<tr>
<td>Silver</td>
<td>34.6 oz. per ton</td>
</tr>
</tbody>
</table>

and is sold to cobalt and nickel refiners. Between December 1905 and February 1913, it is stated that more than

- 40,000,000 ounces of silver,
- 2,200,000 pounds of cobalt,
- 1,500,000 pounds of nickel,
- 4,500,000 pounds of pure white arsenic (As₂O₃),

were produced by the foregoing method.

(b) Oxyde Ores.—Herrenschmidt's method is said to consist in mixing the powdered mineral (wad) to a thin paste with ferrous sulphate solution, and heating to boiling. Sulphates of cobalt, nickel, and manganese pass into solution, whilst iron oxide, silica, and alumina remain behind as an insoluble residue. Thus:

\[ 2\text{FeSO}_4 + \text{MnO}_2 + \text{CoO} = \text{Fe}_2\text{O}_3 + \text{MnSO}_4 + \text{CoSO}_4 \]

\[ 2\text{FeSO}_4 + \text{Co}_2\text{O}_3 = \text{Fe}_2\text{O}_3 + 2\text{CoSO}_4 \]

After filtration, addition of sodium sulphide to the clear solution effects the precipitation of the three metals, cobalt, nickel, and manganese, as sulphides. Digestion with the calculated quantity of ferric chloride oxidises the manganese sulphide to sulphate, which passes into solution. The residue consists of cobalt and nickel sulphides, which are washed and converted into their soluble sulphates by roasting. The sulphates are extracted with water, and converted into chlorides by addition of calcium chloride solution. Their separation is effected as follows: The requisite fraction of the chloride solution is precipitated with milk of lime, and the insoluble hydroxides of nickel and cobalt thus obtained are oxidised to the black hydroxides by treatment with chlorine. The washed precipitate is then introduced into the remainder of the chloride solution and the whole is well stirred and heated, when the black hydrated oxide of nickel passes into solution, displacing the remainder of the cobalt from the solution into the precipitate. The final product is thus a suspension of hydrated peroxide of cobalt in a solution of nickel chloride, from which the cobalt precipitate is removed by filtration, washed, and ignited to the black oxide.

1 Bridges, loc. cit.
II. Purification of Cobalt Oxide

Cobalt oxide obtained by the foregoing methods always contains a little oxide of nickel besides small amounts of other impurities. The following analyses of two Canadian samples of the commercial oxide \(^1\) will serve to illustrate this point:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>70-36</td>
<td>1-12</td>
<td>0-82</td>
<td>0-45</td>
<td>0-10</td>
<td>0-20</td>
<td>0-50</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>(2)</td>
<td>69-2</td>
<td>1-4</td>
<td>0-50</td>
<td>0-54</td>
<td>—</td>
<td>—</td>
<td>0-37</td>
<td>trace</td>
<td>1-46</td>
</tr>
</tbody>
</table>

Since nickel and cobalt closely resemble one another in their general properties, it is, as already stated, generally unnecessary for commercial purposes to effect a complete separation of the two metals. Should such be necessary, however, to obtain a purer oxide of cobalt than the ordinary commercial grade, several methods may be adopted.

The crude oxide is dissolved in hydrochloric acid. To the warm liquor finely divided calcium carbonate is added gradually, with stirring, until no further precipitate is obtained. The precipitate being removed by filtration, the solution is free from iron, arsenic, and silica. The solution is then precipitated with a solution of bleaching powder, \(^2\) added slowly with constant stirring until almost the whole of the cobalt is precipitated as black hydrated oxide. By this means practically none of the nickel is thrown down. The precipitate is washed, dried, and calcined to oxide. It is then boiled with sodium carbonate solution to convert any calcium sulphate into carbonate, and after thorough washing, is treated with very dilute hydrochloric acid to remove the calcium carbonate. Finally the oxide is washed, dried, and calcined.

By treating a crude oxide of composition (1) above in this manner, the product had the following composition \(^1\):

<table>
<thead>
<tr>
<th>Co.</th>
<th>Ni.</th>
<th>Fe.</th>
<th>S.</th>
<th>As.</th>
<th>Ca.</th>
<th>SiO(_2).</th>
</tr>
</thead>
<tbody>
<tr>
<td>71-99</td>
<td>0-041</td>
<td>0-11</td>
<td>0-02</td>
<td>none</td>
<td>0-02</td>
<td>none</td>
</tr>
</tbody>
</table>

It will be observed that practically the whole of the nickel may be removed by this simple process.

When it is necessary to remove the nickel completely, the following processes are available:

1. The preparation of cobalt chloropentammine chloride,

\[
\text{Co}\left[\text{Cl}_{\text{L(NH}_3)_5}\right]\text{Cl}_2,
\]

from solutions of cobalt salts containing nickel has been adopted as a useful commercial method of isolating the cobalt. \(^3\) It is a crystalline salt, reddish violet in colour, nearly insoluble in concentrated hydrochloric acid, and is readily obtained by adding 8 parts of concentrated aqueous ammonia, containing a little ammonium chloride, to 4 parts of crystallised cobalt chloride dissolved in a small quantity of water. After aspirating air through for several hours and then exposing to air

\(^1\) Kalmus, J. Ind. Eng. Chem., 1914, 6, 107.

\(^2\) When fractional precipitation with a hypochlorite is used, and the solution contains sulphate in quantity, sodium hypochlorite should be employed.

for two to three days the mixture assumes a red tint, whereupon it is acidified with hydrochloric acid, and a voluminous precipitate of the cobaltammine is obtained. This is washed with aqueous hydrochloric acid, and may be worked up into any desired cobalt salt. Any nickel present in the original solution remains unaltered, a complete separation of the two metals being thus effected.

(2) Cobalt chloride readily dissolves in ether saturated with hydrogen chloride, yielding a blue solution. Nickel chloride, on the contrary, is insoluble, being precipitated as the yellow, anhydrous salt. The separation of nickel from cobalt chloride may thus be effected as follows:

A kilogram of crystallised cobalt chloride, already freed from metals other than nickel, is dissolved in 1600 grams of concentrated hydrochloric acid and poured into 6 litres of ether saturated with hydrogen chloride. After filtration the ether is evaporated off, leaving a residue of cobalt chloride.¹

(3) Fischer's Nitrite Process hinges on the fact that when potassium nitrite is added in excess to a solution of a cobalt salt containing free acetic acid, a yellow precipitate of potassium cobaltii-nitrite is obtained. Nickel does not yield an insoluble salt under these conditions, and an effective separation of the two metals may thus be made.²

(4) Mond's Process.—A very complete separation of nickel from cobalt may be effected by reducing to the metallic condition and removing the nickel in the form of volatile nickel carbonyl by heating in a current of carbon monoxide.³ Cobalt does not yield a carbonyl under the same conditions.

III. Preparation of Metallic Cobalt from its Oxide

Commercial oxide of cobalt, as obtained from the smelters, consists essentially of cobalto-cobaltic oxide, Co₃O₄, and a careful study has been made by Kalmus⁴ of the conditions under which this oxide may be reduced to metallic cobalt.

(1) Reduction of the Oxide with Carbon.—By heating cobalto-cobaltic oxide with carbon in a furnace reduction ensues, carbon monoxide or dioxide or a mixture of the two being evolved according to circumstances. Thus:

\[
\begin{align*}
\text{Co}_3\text{O}_4 + 4\text{C} & \rightarrow 3\text{Co} + 4\text{CO} \\
\text{Co}_3\text{O}_4 + 4\text{CO} & \rightarrow 3\text{Co} + 4\text{CO}_2.
\end{align*}
\]

Charcoal and lampblack effect the reduction more easily than anthracite, complete reduction being effected with the former at 900° C., some 20 to 30 per cent. of charcoal in excess of that required in the above equation being desirable. At higher temperatures the reduction proceeds much more rapidly. By briquetting the charcoal and cobalt oxide, using some organic material, such as molasses, as binder, reduction may be effected at a slightly lower temperature.

In the commercial production of cobalt the oxide is usually heated with charcoal in the manner described for nickel.

¹ Pinerua, Compt. rend., 1897, 124, 862.
² See p. 60.
³ Details of Mond's process are given on pp. 87–88.
(2) Reduction of the Oxide with Hydrogen.—This begins at 190° to 200° C., and proceeds easily at 250° C. Between 500° and 700° C. more than 90 per cent. of the oxide is reduced in a few minutes, but further reduction is slow. As the temperature rises the reduction becomes more rapid and complete, whilst at 1100° C. it is rapidly completed. The cobalt must be cooled in hydrogen as it is very susceptible to oxidation. For the production of a pure, carbon-free metal this method is recommended.²

(3) Reduction of the Oxide with Carbon Monoxide.—Reduction of cobalto-cobaltic oxide to the metal takes place rapidly, and is quite complete at 900° C. Between 850° and 450° C. the reaction is very interesting. At first some oxide is reduced to metallic cobalt; after a time the finely divided metal decomposes the carbon monoxide, depositing solid carbon, presumably in the same way as its analogue, iron, namely:

\[ \text{Co} + 2\text{CO} = \text{Co} + \text{C} + \text{CO}_2. \]

At about 600° C. the cobalto-cobaltic oxide is reduced to cobaltous oxide, CoO, and if this is removed from the furnace and exposed to the air it becomes incandescent in consequence of re-oxidation to the higher oxide:

\[ 6\text{CoO} + \text{O}_2 = 2\text{Co}_3\text{O}_4. \]

(4) Reduction of the Oxide with aluminium.—This is known as Goldschmidt's process, and hinges upon the fact that the heat of formation of aluminium oxide is 392·6 kilogram calories,³ which is higher than that of most other metallic oxides⁴—in other words, aluminium is capable of reducing such oxides to the free metal by reason of its greater avidity or attraction for their oxygen.⁵ The heat of formation of Co₃O₄ is 193·4 cals. Now to reduce three molecules of cobalto-cobaltic oxide to metal requires 3 × 193·4 = 580·2 cals. Thus:

\[ 3\text{Co}_3\text{O}_4 = 9\text{Co} + 6\text{O}_2 - 580·2 \text{ cals.} \]

By oxidising 8 atoms of aluminium to 4 molecules of oxide, 4 × 392·6 = 1570·4 cals. are liberated. Thus:

\[ 8\text{Al} + 6\text{O}_2 = 4\text{Al}_2\text{O}_3 + 1570·4 \text{ cals.} \]

Combining equations (i) and (ii) we have:

\[ 3\text{Co}_3\text{O}_4 + 8\text{Al} = 9\text{Co} + 4\text{Al}_2\text{O}_3 + 990·2 \text{ cals.} \]

In other words, the reaction is strongly exothermic and, when once started with an ignition powder such as a fuse of finely divided aluminium and potassium chlorate wrapped in paper (Kalmus), will proceed very vigorously to completion. The metal may be produced in this way in a very pure form containing less than 0·1 per cent. of aluminium and, of course, entirely free from carbon.

**Preparation of Cobalt by Electrolytic Methods.**

Cobalt may be obtained by the electrolysis of aqueous solutions of cobalt sulphate containing ammonium sulphate and hydroxide, using a platinum cathode and anode.

2 Kalmus, *loc. cit.*
3 For notes on thermo-chemistry see this Series, Vol. I, 2nd ed., 1917, p. 163.
4 Per equivalent of oxygen.
5 This is the principle of the reactions with thermit. See this Series, Vol. IV, p. 58,
In preparing a specimen of the pure metal for atomic weight determinations, Winkler found the following solution useful:

100 c.c. cobalt sulphate solution, containing 11·62 grams of cobalt per litre,
30 grams ammonium hydroxide of density 0·905,
500 c.c. water,

employing a current density of 0·6 amperes.

The metal obtained in this way contains a small quantity of oxide, but this may be reduced by heating in a current of hydrogen gas.¹

Preparation of Cobalt in the Laboratory.—For laboratory purposes cobalt may readily be obtained by reduction of its oxides by hydrogen at temperatures above 250° C.; by heating the chloride ² or purpureo salt ³ to redness in a current of the same gas; and by calcining the oxalate either in a closed vessel or in an atmosphere of hydrogen.⁴ This third method invariably yields a slightly carburised metal. Cobalt may be obtained in the wet way by precipitation from faintly acid solutions of its salts by metallic magnesium, as also from ammoniacal solutions with metallic zinc.⁵

Electrolytic reduction of the double cobalt ammonium sulphate⁶ in the presence of ammonium hydroxide, or of the double oxalate in the presence of excess of ammonium oxalate, yields a very pure metal.

Pyrophoric Cobalt was described by Magnus in 1825,⁷ who prepared it by reduction of its oxides in a current of hydrogen. The best temperature of reduction ⁸ appears to be 250° C. If the reduction is effected at 700° C. the cobalt is not pyrophoric. Pyrophoric cobalt is a black powder, which burns brilliantly when exposed to the air in consequence of rapid oxidation.

Physical Properties.—Cobalt is a silver-white metal which, when pure, may be machined in a lathe as readily as pure nickel or pure iron. The commercial metal, containing small percentages of carbon, machines after the manner of mild steel. When under corresponding conditions cobalt is harder than nickel and iron.⁹ The effect of carbon between 0·06 and 0·87 per cent. is not sufficient to counteract that of slight variations in the heat treatment. The tensile strength of cobalt when pure, cast, and unannealed is 34,400 lb. per square inch, which value is increased to 59,700 lb. with a carbon content of 0·062 per cent.; and to 61,900 lb. when the carbon reaches 0·25 per cent.

The specific electric resistance of cobalt wires of great purity is 89·64 × 10⁻⁷ ohms per cm. cube, but this value increases enormously by the addition of small quantities of impurities.

¹ Winkler, Zeitsch. anorg Chem., 1895, 8, 1. See also Besquerel, Compt. rend., 1862, 55, 18; Boisbandran, ibid., 1871, 73, 1222; Mansfeld, Zeitsch. anal. Chem., 1877, 16, 344; Wohl, ibid., 1879, 18, 523; Fresenius and Bergmann, ibid., 1880, 19, 314; Schlucht, ibid., 1883, 22, 493.
² Peligot, Compt. rend., 1844, 19, 670.
³ Sharswood, Monit. Scient., 1859, 2, 889.
⁶ See p. 34.
Cobalt is magnetic at all temperatures up to about 1150° C., at which point it becomes non-magnetic.\textsuperscript{1} When placed in a magnetic field a bar of cobalt increases in length,\textsuperscript{2} and it is interesting to note in this connection that this magnetic elongation for both cast and annealed cobalt becomes practically nil between 1100° and 1200° C.\textsuperscript{3}

The density of pure cobalt containing 99.9 per cent. of the metal and a trace of iron, but no nickel or carbon, is given as follows\textsuperscript{4}:

<table>
<thead>
<tr>
<th>Condition of metal</th>
<th>Density.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast from just above the melting-point (c. 1500° C.)</td>
<td>8.7562 at 15° C.</td>
</tr>
<tr>
<td>Cast and swaged down to a thin cylindrical bar</td>
<td>8.9227 at 19° C.</td>
</tr>
<tr>
<td>Cast and annealed from 700° C.</td>
<td>8.8105 at 14.5° C.</td>
</tr>
</tbody>
</table>

From the foregoing it is evident that the mechanical history of the metal has an important influence upon its density, as is usually the case.

The density of pure electrolytic cobalt foil is given by Winkler\textsuperscript{5} as 7.9678 at 20° C.\textsuperscript{6}

The coefficient of linear expansion of cobalt is given by the expression:

$$\alpha = 0.00001208 + 0.000,000,0128t$$

between 6° and 121° C.\textsuperscript{7}

The melting-point of cobalt has been determined by a considerable number of investigators, the most reliable results being as follow\textsuperscript{8}:

<table>
<thead>
<tr>
<th>Melting-point, °C.</th>
<th>Authority.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1478 ± 1.1</td>
<td>Kalmus and Harper, \textit{opus cit.}</td>
</tr>
<tr>
<td>1477, 1478</td>
<td>Burgess and Waltenberg, \textit{Bureau Standards}, Washington, 1913, 10, 13; 1912, 9, 475.</td>
</tr>
<tr>
<td>1464</td>
<td>Burgess, \textit{ibid.}, 1907, 3, 350.</td>
</tr>
</tbody>
</table>

\textsuperscript{1} Guertler and Tammann, \textit{Zeitsch. anorg. Chem.}, 1904, 42, 353.
\textsuperscript{3} Honda and Schimizu, \textit{Phil. Mag.}, 1903, [vi], 6, 392.
\textsuperscript{5} Winkler, \textit{Zeitsch. anorg. Chem.}, 1895, 8, 1.
\textsuperscript{8} Other values are given by Copaux, \textit{loc. cit.}; Guertler and Tammann, \textit{Zeitsch. anorg. Chem.}, 1904, 42, 353; 1905, 45, 223; Carnalley, \textit{Ber.}, 1879, 12, 441; Pictet, \textit{Compt. rend.}, 1879, 88, 1317.
Cobalt boils at 2415° C. under 30 mm. pressure. Its specific heat has been determined by numerous investigators, the more important results being as follow:

<table>
<thead>
<tr>
<th>Specific heat</th>
<th>Temperature range, °C</th>
<th>Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10795</td>
<td>20–100</td>
<td>Schmitz, <em>Proc. Roy. Soc.</em>, 1908, 72, 177.</td>
</tr>
<tr>
<td>0.1053</td>
<td>15–100</td>
<td>Kalmus and Harper, <em>opus cit.</em>, p. 43.</td>
</tr>
<tr>
<td>0.1056</td>
<td>15–100</td>
<td>Drisko, quoted by ditto, p. 43.</td>
</tr>
<tr>
<td>0.104</td>
<td>20–100</td>
<td>Copaux, <em>loc. cit.</em></td>
</tr>
<tr>
<td>0.103</td>
<td>15–100</td>
<td>Tilden, <em>Proc. Roy. Soc.</em>, 1900, 66, 244; 1903, 71, 220.</td>
</tr>
</tbody>
</table>

The specific heat at any temperature between 0° and 890° C. may be calculated from the equation:

\[
\text{Specific Heat} = 0.1058 + 0.0457t + 0.0466t^2.
\]

The most intense lines in the spectrum of cobalt are as follow:


**Occlusion of Hydrogen by Cobalt.**—Hydrogen is readily occluded by cobalt to an extent dependent upon a variety of factors. Chief amongst these are:

1. **Temperature.**—Cobalt slowly occludes hydrogen in the cold, but at its temperature of reduction, namely, 400° to 500° C., its occluding power is negligible. At some intermediate temperature occlusion progresses at a maximum rate. Cobalt obtained by reduction in hydrogen but cooled in nitrogen occludes an inappreciable quantity of hydrogen.

2. **Length of Exposure.**—The amount of occluded hydrogen tends towards a maximum with increasing length of exposure of the metal to that gas.

3. **Physical Condition of the Metal.**—The more finely divided the metal the greater is its power of occluding hydrogen. This probably explains many of the apparently anomalous results detailed in the literature on the subject. Thus, for example, cobalt reduced from the bromide does not possess the property of occluding hydrogen to any important extent. The metal obtained, on the other hand, by reduction from its oxides contains varying amounts of the gas. Reduced at

---

COBALT AND ITS COMPOUNDS

400° C., Troost and Hautefeuille \(^1\) found it to contain approximately 100 times its volume of hydrogen, with which it readily parted upon heating to 200° C. \textit{in vacuo}. The explanation appears to be that the volatility of cobalt bromide allows the metal to be deposited, upon reduction, in a more compact form than that obtained from the oxide, so that its occluding power is proportionately reduced.\(^2\)

Neumann and Streintz \(^3\) observed that repeated oxidation and reduction tends to diminish the power of cobalt to occlude hydrogen. As Baxter has pointed out, this is probably due to the fact that these operations tend to render the cobalt increasingly compact. The presence of impurities does not appear to affect very materially the occluding powers of cobalt.

**Chemical Properties.**—Cobalt is not sensibly altered by exposure to air or water at ordinary temperatures, but becomes superficially oxidised at red heat.\(^4\) After being maintained at red heat for some time in an atmosphere of pure nitrogen, the metal becomes less susceptible to attack by nitric acid, possibly because of the formation of a "passive" nitride.\(^5\)

Cobalt thus resembles iron in exhibiting passivity, although to a less extent. Concentrated nitric acid attacks it, but acid in the proportion of one part water with two parts concentrated acid dissolves cobalt with extreme slowness.\(^6\)

The metal dissolves slowly in hydrochloric acid in dilute sulphuric acid, evolving hydrogen. It combines with chlorine and bromine under the influence of heat, yielding the anhydrous chloride and bromide respectively. Neither cold nor hot solutions of sodium or potassium hydroxide attack cobalt unless the metal is simultaneously made an anode.\(^7\)

Heated in ammonia to about 470° C. cobalt yields a nitride which decomposes at 600° C. Heated in nitrogen peroxide it burns with incandescence, yielding cobalto-cobaltite oxide, \(\text{Co}_2\text{O}_4\).\(^8\)

Electrolytic cobalt does not contain nitrogen, and yields no ammonia on heating in a current of pure hydrogen, thereby differing from its congeners, iron and nickel.

When obtained in a finely divided state by reduction of its oxides at 250° C. cobalt is pyrophoric. In this condition it decomposes acetylene in the cold, the metal becoming incandescent. A portion of the acetylene polymerises to benzene, whilst the remainder yields carbon and hydrogen.\(^9\)

Reduced at 400° C. the metal is not pyrophoric, but occludes a considerable volume of hydrogen. The reduced metal decomposes carbon monoxide at 850° to 450° C., depositing solid carbon. Thus:

\[
\text{CO} + 2\text{CO} = \text{Co} + \text{CO}_2 + \text{C}.
\]

In this respect, again, cobalt closely resembles iron.

---

\(^1\) Troost and Hautefeuille, \textit{Compt. rend.}, 1875, 90, 788.


\(^3\) Neumann and Streintz, \textit{Monash.}, 1891, 12, 642.


\(^7\) Tubandt, \textit{Zeitsch. anorg. Chem.}, 1905, 45, 368.

\(^8\) Sabatier and Senderens, \textit{Bull. Soc. chim.}, 1903, 29, 294.

The metal also combines under special conditions with nitrogen peroxide to form nitro-cobalt, \( \text{Co}_2(\text{NO}_3)_4 \). When heated with silicon in the electric furnace, silicides are produced, whilst warming with carbon monoxide under pressure effects the production of cobalt tetracarbonyl, \( \text{Co(CO)}_4 \). Heated in nitric oxide to 150° C. the metal burns, yielding the monoxide; at red heat it decomposes steam.

"Asymmetry" of the Cobalt Atom.—Optically active compounds of cobalt have been produced, indicating that their structure is asymmetric.

Atomic Weight.—Approximate Atomic Weight.—That the atomic weight of cobalt is approximately 59 and not a multiple or submultiple of this amount is evident from a variety of considerations, namely:

1. The specific heat of cobalt is 0·108. Assuming a mean atomic heat of 6·4, the atomic weight, according to Dulong and Petit's Law, is approximately 59-8.
2. The most appropriate position for cobalt in the Periodic Table is, as explained in the opening chapter of this volume, between iron and nickel. Assuming the atomic weights of iron and nickel to be correct, we should expect the value for cobalt to be greater than 55·84 (at. wt. of iron), but less than 58·68 (at. wt. of nickel).
3. The cobalt alums are isomorphous with those of iron and aluminium, and therefore, by the application of Mitscherlich's Law, they must be assumed to contain two atoms of cobalt, their generic formula being:

\[ \text{M}_2\text{SO}_4 \cdot \text{Co}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}. \]

Again, double cobaltous sulphates with alkali sulphates are isomorphous with those of nickel and divalent iron, from which it may similarly be gathered that their formulae are given by the generic scheme:

\[ \text{M}_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}. \]

Analyses of these compounds indicate that the atomic weight of cobalt is 59-0.

Exact Atomic Weight.—Until 1857 the accepted value for the atomic weight of cobalt was derived from a single experiment made by Rothoff in 1826; 269·2 parts of CoO were found to be equivalent to 1029·9 of AgCl, whence Co = 58·9.

In 1857, Schneider analysed cobalt oxalate, determining the carbon dioxide obtained by its combustion and the metal left after igniting the salt in air and subsequently in hydrogen. Four analyses gave the following result:

\[ \text{Co} : 2\text{CO}_2 : 100·000 : 146·665 \quad \text{whence Co} = 60·005 \]

The following year Marignac made a number of preliminary experiments on the atomic weight of cobalt. In two experiments anhydrous cobalt sulphate was calcined to oxide:

\[ \text{CoSO}_4 : \text{CoO} : 100·000 : 48·287 \quad \text{Co} = 58·761 \]

1 Werner, Ber., 1914, 47, 3087.
2 All atomic weights quoted in this section have been recalculated, using the following antecedent data: O = 16·000, H = 1·00782, C = 12·003, N = 14·008, S = 32·065, Cl = 35·457, Br = 79·916, I = 126·92, Ag = 107·880, Au = 197·2.
3 See Berzelius, Pogg. Annalen, 1826, 8, 184.
5 Marignac, Arch. Sci. phys. nat., 1858, 1, 372.
In another four experiments anhydrous cobalt chloride was analysed for chlorine by titration with silver:

\[2\text{Ag} : \text{CoCl}_2 : \overline{100-000 : 60-118} \quad \text{whence} \quad \text{Co} = 58-797\]

In 1860 Dumas' analyses of anhydrous cobalt chloride appeared.\(^1\) Five analyses gave the following mean result:

\[2\text{Ag} : \text{CoCl}_2 : \overline{100-000 : 60-228} \quad \text{Co} = 59-034\]

In 1863 Russell\(^2\) reduced pure cobaltous oxide to the metal in a stream of hydrogen, and as the mean of fifteen experiments obtained the following result:

\[\text{CoO} : \text{Co} : \overline{100-000 : 78-592} \quad \text{Co} = 58-738\]

Three years later, Sommaruga\(^3\) made seven analyses of purpureo-cobaltic chloride by heating it until cobaltous chloride remained, and reducing this salt in a stream of hydrogen:

\[\text{Co(NH}_3)_5\text{Cl}_3 : \text{Co} : \overline{100-000 : 23-827} \quad \text{Co} = 59-909\]

In 1867 Winkler\(^4\) made five determinations of the amount of gold precipitated from sodium aurichloride solution by a given weight of cobalt:

\[2\text{Au} : 3\text{Co} : \overline{100-000 : 45-172} \quad \text{Co} = 59-386\]

In 1869, Russell\(^6\) redetermined the atomic weight of cobalt by dissolving the metal in hydrochloric acid and measuring the hydrogen evolved. Computing his results with the modern value for the density of hydrogen, his eleven experiments give the following mean result:

\[\text{Co} : \text{H}_2 : \overline{100-000 : 3-4112} \quad \text{Co} = 59-077\]

In 1871, Lee\(^7\) determined the percentage of cobalt in brucine cobalti-cyanide, strychnine cobalti-cyanide, and purpureo-cobaltic chloride:

\[(\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2)\text{H}_3\text{Co(CN)}_6 \cdot 4\text{H}_2\text{O} : \text{Co} : \overline{100-000 : 3-7437} \quad \text{Co} = 59-199\]
\[(\text{C}_{22}\text{H}_{28}\text{N}_4\text{O}_4)\text{H}_3\text{Co(CN)}_6 \cdot 10\text{H}_2\text{O} : \text{Co} : \overline{100-000 : 8-4112} \quad \text{Co} = 58-839\]
\[\text{Co(NH}_3)_5\text{Cl}_3 : \text{Co} : \overline{100-000 : 23-5795} \quad \text{Co} = 59-095\]

In 1886, Zimmermann\(^8\) made ten extremely concordant analyses of cobaltous oxide by reducing it to the metal in a stream of hydrogen:

\[\text{CoO} : \text{Co} : \overline{100-000 : 78-635} \quad \text{Co} = 58-324\]

\(^1\) Dumas, Annalen, 1860, 113, 25.
\(^3\) Sommaruga, Sitzungber. K. Akad. Wiss. Wien, 1866, 54, 50; see also Schneider, Pogg. Annalen, 1866, 130, 310.
\(^4\) Winkler, Zeitsch. anal. Chem., 1867, 6, 18.
\(^5\) Weselsky, Ber., 1868, 2, 592.
\(^7\) Lee, Amer J. Sci., 1871, [iii], 2, 44.
\(^8\) Zimmermann, Annalen, 1886, 232, 324.
Another series of twenty-four experiments on the reduction of cobaltous oxide was published shortly afterwards by Remmler:

\[ \text{CoO} : \text{Co} : 100-000 : 78.613 \quad \text{whence} \quad \text{Co} = 59.812 \]

In 1898–1899, Winkler published the results of his experiments on the atomic weight of cobalt. First, pure cobalt was converted into the neutral chloride, and in six experiments the chloride determined gravimetrically as silver chloride:

\[ 2\text{AgCl} : \text{Co} : 100-000 : 20.364 \quad \text{Co} = 59.812 \]

In a second series of six experiments the chloride was determined volumetrically by Volhard’s method after removing the cobalt with potassium carbonate. The ratio of cobalt to silver was thus established and checked by two experiments in which cobalt was allowed to displace silver from silver sulphate solution:

\[ 2\text{Ag} : \text{Co} : 100-000 : 27.705 \quad \text{Co} = 59.776 \]

In a third series of eight experiments a weighed amount of cobalt was dissolved in excess of a standard solution of iodine in potassium iodide, the excess of iodine being then titrated with sodium thiocyanate:

\[ \text{I}_2 : \text{Co} : 100-000 : 28.462 \quad \text{Co} = 59.556 \]

In 1895, Hempel and Thiele’s determinations appeared. Three experiments on the reduction of cobaltous oxide gave the following result:

\[ \text{CoO} : \text{Co} : 100-000 : 78.666 \quad \text{Co} = 58.998 \]

In another series of seven experiments a weighed amount of cobalt was converted into the anhydrous chloride, and the increase in weight noted:

\[ \text{Cl}_2 : \text{Co} : 100-000 : 82.873 \quad \text{Co} = 58.769 \]

Finally, in four of the preceding experiments the chlorine in the anhydrous chloride was estimated as silver chloride:

\[ 2\text{AgCl} : \text{Co} : 100-000 : 20.556 \quad \text{Co} = 58.929 \]

The foregoing results are of little or no value in comparison with those that have been subsequently obtained. They vary considerably, but undoubtedly point to a value round about 59 for the atomic weight of cobalt. The results obtained by Schneider, Sommaruga, and Winkler are much higher than all the others, and it will be noticed that in the hands of Lee, Sommaruga’s method gave a much lower value.

In 1897–1899, the work of Richards and Baxter on the atomic weight of cobalt was published. Anhydrous cobaltous bromide was prepared by direct union of the pure elements and the product sublimed in a stream of hydrogen bromide and nitrogen. The bromine in the salt was determined by the two usual methods, the amount of silver required to precipitate it being first measured and then the precipitated silver bromide being collected and weighed. The final results were as follow:

<table>
<thead>
<tr>
<th>Experiments</th>
<th>[ 2\text{Ag} : \text{CoBr}_2 : 100-000 : 101.407 ]</th>
<th>\text{Co} = 58.964</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 expts.</td>
<td>[ 2\text{AgBr} : \text{CoBr}_2 : 100-000 : 58.255 ]</td>
<td>\text{Co} = 58.969</td>
</tr>
</tbody>
</table>

1 Remmler, Zeitseh. anorg. Chem., 1892, 2, 221.
3 Hempel and Thiele, Zeitseh. anorg. Chem., 1895, 11, 73.
These results were confirmed by a series of experiments in which
the anhydrous bromide was reduced to metallic cobalt by heating it
in hydrogen. Twelve experiments gave the following mean result:

\[
\text{CoBr}_2 : \text{Co} : : 100 : 000 : 26:952 \quad \text{whence} \quad \text{Co} = 58.972
\]

It is seen that the atomic weight thus obtained is practically the
same as that derived from the percentage of bromine in the salt, an
indication of the high degree of accuracy of the experimental work.

Richards and Baxter also analysed the chloride and oxide of cobalt.
It was not found possible to prepare the anhydrous chloride wholly
free from alkali chloride and silica, so that their two reductions of
the chloride to the metal are slightly in error:

\[
\text{Cl}_2 : \text{Co} : : 100 : 000 : 88.266 \quad \text{Co} = 59.047
\]

The analyses of cobaltous oxide were also regarded with suspicion,
owing to the difficulty of ascertaining whether the oxide is free from
excess of oxygen. Five experiments were made:

\[
\text{CoO} : \text{Co} : : 100 : 000 : 78.659 \quad \text{Co} = 58.973
\]

With the subsequent invention of fused quartz vessels it became
possible to prepare pure anhydrous cobalt chloride. Accordingly, in
1906, Baxter and Coffin \(^1\) prepared and analysed this salt in the cus-
tomary Harvard manner, the results being as under:

\[\begin{array}{ll}
8 \text{ expts.} & 2\text{Ag} : \text{CoCl}_2 : : 100 : 000 : 60.1975 \quad \text{Co} = 58.968 \\
7 \text{ expts.} & 2\text{AgCl} : \text{CoCl}_2 : : 100 : 000 : 45.8070 \quad \text{Co} = 58.969
\end{array}\]

The excellent agreement between Richards and Baxter’s analyses
of cobalt bromide and Baxter and Coffin’s analyses of cobalt chloride
leaves no doubt as to the accuracy of the value

\[
\text{Co} = 58.97
\]

for the atomic weight of cobalt, and this is the value given in the
International Committee’s table for 1918.

Uses.—Cobalt has not hitherto been utilised to any important
extent in the industries, but Canada is making systematic efforts to
develop its utility in view of the fact that rich stores of cobalt ores are
found in that country. A few years ago practically the only use for
cobalt was the production of the blue colour in the glass and ceramic
industries, and for the production of a blue paint. For these industries
an annual production of 800 or 400 tons of cobalt sufficed.\(^2\)

Two important fields suggest themselves as offering useful possi-
bilities for the future, namely, electroplating and currency. The former
of these is discussed in the next section. With regard to the latter it
has been pointed out \(^3\) that a five-cent piece made of cobalt would
possess many advantages for Canadian currency. Being very hard it
would be difficult to counterfeit, while its attractive colour and resistance
tarnishing would distinguish it from all other coins.

Several compounds of cobalt are of considerable importance, chief
amongst which are zaffre, smalt, and cobalt blue. Accounts of these
are given in the sequel. Certain organic derivatives of cobalt, such as

\(^1\) Baxter and Coffin, \textit{J. Amer. Chem. Soc.}, 1906, 28, 1580; \textit{Chem. News}, 1907, 95,
76, 86.
the rosinate, oleate, linoleate, and tungate, find commercial application as "driers" in the paint and varnish industry. The acetate and oxide also exert an appreciable drying action.

Owing to their change of colour under varying conditions of hydration, cobalt salts have long been used in the preparation of "sympathetic inks."

**Electro-deposition of Cobalt.**—Although nickel has been very largely used for commercial electroplating purposes, there would appear to be a useful field for a cobalt electroplate industry. The earlier literature on the subject is full of contradictions, but this is readily understood when it is remembered what an important influence upon the nature of deposited metals is exerted by different factors such as temperature, current density, chemical composition of the solution employed, etc.

A solution of a cobalt salt, or a mixture of salts containing cobalt, is prepared and a cobalt anode inserted. The carefully cleaned article to be plated is introduced as cathode, and a suitable current passed through the system.

It is most important that the anode shall consist of cobalt in a high state of purity. In view of the improvements in the metallurgy of that metal, this condition is not now an insuperable barrier to success as a very pure metal may now be obtained on a commercial scale. The anodes may be either cast or rolled sheet according to whichever is the more convenient or more easily obtainable. The difference between the two is not so important as in the case of nickel, since cobalt dissolves rather more readily; the anodes, however, should be annealed and thoroughly cleansed before use.

The problem of a suitable solution has long been a matter of discussion. Sylvanus Thompson in 1887 recommended and patented the following mixtures:

\[
\begin{align*}
\text{Cobalt ammonium sulphate} & \quad 1 \text{ lb. or } 500 \text{ grams} \\
\text{Magnesium sulphate} & \quad \frac{1}{2} \text{ lb. or } 250 \\
\text{Ammonium sulphate} & \quad \frac{1}{3} \text{ lb. or } 250 \\
\text{Citric acid} & \quad 1 \text{ oz. or } 31.2 \\
\text{Water} & \quad 1 \text{ imperial gallon or } 5 \text{ litres} \\
& \quad 1\frac{1}{3} \text{ U.S. gallons}
\end{align*}
\]

and

\[
\begin{align*}
\text{Cobalt sulphate} & \quad 1 \text{ lb. or } 250 \text{ grams} \\
\text{Magnesium sulphate} & \quad \frac{1}{2} \text{ lb. or } 125 \\
\text{Ammonium sulphate} & \quad \frac{1}{3} \text{ lb. or } 125 \\
\text{Water} & \quad 1 \text{ imperial gallon or } 5 \text{ litres} \\
& \quad 1\frac{1}{4} \text{ U.S. gallons}
\end{align*}
\]

These solutions yield their optimum results at about 35° C. A simple solution, rapidly made up, consists of:

\[
\begin{align*}
\text{Cobalt potassium sulphate} & \quad 1 \text{ lb.} \\
\text{Water} & \quad 1 \text{ imperial gallon}
\end{align*}
\]

1 For further details see *A Treatise on Electro-Metallurgy*, McMillan and Cooper (Chas. Griffin and Co., 1910); *Electroplating*, Barclay and Hainsworth (Arnold, 1912); *Applied Electrochemistry*, Allmand (Arnold, 1912).

and its efficiency is increased by the addition of approximately 1 oz. of sodium hypophosphite.

For these solutions a cathode current density of $1\frac{1}{2}$ amperes per square foot is recommended, although for the first few seconds of immersion a little higher current may be applied, but should be quickly reduced. The voltage may advantageously lie in the neighbourhood of 2 volts.

Kalmus and his co-workers 2 recommend the following compositions:

1. A solution of 200 grams of cobalt ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4\cdot\text{CoSO}_4\cdot6\text{H}_2\text{O}$, equivalent to 145 grams of the anhydrous salt, in one litre of water. The density of the solution is 1·058 at 15° C.

This solution is useful at all current densities up to 4 amperes per sq. dm. or 37·2 amperes per sq. foot.

2. A solution in one litre of water of the following:

- Cobalt sulphate, $\text{CoSO}_4$ . . . . . . . . 312 grams
- Sodium chloride, $\text{NaCl}$ . . . . . . . . 19·6
- Boric acid, $\text{H}_3\text{BO}_3$ . . . . . . . . nearly to saturation

The density of the above solution is 1·25 at 15° C.

This solution plates most satisfactorily with a current density ranging from 3·5 to 26·4 amperes per sq. dm., the latter figure being equivalent to over 240 amperes per sq. foot; and even at this speed the limit of the solution is not reached. The solution does not change appreciably either in cobalt content or in acidity over long periods of time, and is thus particularly useful for commercial practice.

The following conclusions are arrived at by Kalmus:

1. The electro-deposition of cobalt from either of the foregoing solutions on to brass, iron, steel, copper, tin, lead, Britannia metal, and German silver may be effected under conditions similar to those employed for nickel. The deposit is firm, adherent, hard, and uniform. It is readily buffed to a finished surface having a beautiful lustre, possessing a slightly bluish cast, although beautifully white.

2. The deposit is much harder than nickel, so that less weight (about one-fourth) is needed for equal protection. The plating satisfactorily withstands the various hammering, bending, and burnishing tests usually applied.

3. The electric-conductivity of the cobalt solutions is considerably higher than that of commercial nickel solutions. Other things being equal, therefore, the cobalt solutions may be worked at a lower voltage for a given speed of plating; or solution (1) may be worked four times, and solution (2) some fifteen times as fast as the most rapid nickel solution.

Other workers, who have had occasion to repeat the work of Kalmus report considerable difficulty in obtaining thick deposits of cobalt consistent with a high quality of adhesion. The solutions recommended by Kalmus yield quite satisfactory results for very thin deposits, but the case is otherwise where deposits are required ranging in thickness from 3 to 5 thousandths of an inch and upwards. In these cases the deposited metal is found to separate very readily from its base. 3

Furthermore, in view of more recent research on the rapid deposition

1 W. R. Barclay, private communication.

of nickel (see p. 102), it would appear that the possibilities of improve-
ment in this direction have by no means been exhausted. Consequently
the third conclusion of Kalmus relating to the relative speeds of deposi-
tion of cobalt and nickel may shortly require revision.

From the foregoing it is evident that the whole subject is worthy of
further careful commercial investigation.

ALLOYS OF COBALT

Other useful fields for the employment of cobalt are offered by its
alloys.

Cobalt has been successfully used in the manufacture of high-speed
steels, in which some 4 per cent. of cobalt is employed, in addition to
chromium and tungsten. Stellite, an alloy containing 75 per cent. of
cobalt, the remainder being chromium (usually with a little tungsten),
is hard and remarkably resistant to ordinary corroding agents. It is
therefore in demand for the so-called "stainless" cutlery. Cochrome
is an alloy similar to nicherome, save that the nickel in the latter is
replaced by cobalt. It has a higher melting-point than nicherome, is
less readily oxidised, and in these respects is superior to it for purposes
of electric heating. Cobalt amalgam is used in dentistry.

Apart from the foregoing, cobalt yields no alloys of any great
commercial importance. The following table indicates those that have
been made the subject of more or less careful study:

<table>
<thead>
<tr>
<th>Elements alloying with Cobalt</th>
<th>Remarks</th>
<th>Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium . . . .</td>
<td>CoAl, Co₂Al₅, and Co₃Al₇ have been obtained.</td>
<td>O. Brunck, Ber., 1901, 34, 2733.</td>
</tr>
<tr>
<td>Arsenic . . . .</td>
<td>See p. 65.</td>
<td>Schirmeister, Metallurgie, 1911, 8, 650.</td>
</tr>
<tr>
<td>Bismuth . . . .</td>
<td>Limits of miscibility in liquid state are 6 and 93 per cent. Of cobalt. No evidence of compounds.</td>
<td>—</td>
</tr>
<tr>
<td>Chromium . . . .</td>
<td>Miscible in all proportions both in liquid and in solid state.</td>
<td>Lewkonja, Zeitsch. anorg. Chem., 1908, 59, 293.</td>
</tr>
</tbody>
</table>
| Chromium and molybd-
| | | Lewkonja, loc. cit. |
| | | Haynes, loc. cit. |

2 "It is claimed that this metal is to high-speed steel what high-speed steel is to ordinary carbon steel; that is, it will allow of increasing the rate of cutting on the lathe from 20 per cent. to 50 per cent. and minimises the time consumed in sharpening tools" (J. Soc. Chem. Ind., 1917, 36, 441).
<table>
<thead>
<tr>
<th>Elements alloying with Cobalt</th>
<th>Remarks</th>
<th>Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>No definite compound exists. Completely miscible in fused state. Alloys containing 99 per cent. copper are still magnetic. Those with more than 70 per cent. copper have a red tint; those with less than 10 per cent. copper are grey and similar to cobalt.</td>
<td>Ducelliez, <em>Bull. Soc. chim.</em>, 1910, 7, 158.</td>
</tr>
<tr>
<td>Gold</td>
<td>No compounds. Saturated solid solutions contain 3-5 and 94 per cent. of gold respectively.</td>
<td>Säbman, <em>Zeitsch. anorg. Chem.</em>, 1908, 57, 1.</td>
</tr>
<tr>
<td>Manganese</td>
<td>Continuous series of solid solutions. Alloys with more than 40 per cent. cobalt are markedly magnetic, this property increasing with cobalt content.</td>
<td>Neuburger, <em>Elektrochem. Zeitsch.</em>, 1914, 20, 295.</td>
</tr>
<tr>
<td>Silicon</td>
<td>See p. 72.</td>
<td>—</td>
</tr>
<tr>
<td>Zinc</td>
<td>Evidence of compound CoZn₄.</td>
<td>—</td>
</tr>
</tbody>
</table>

COMPOUNDS OF COBALT

General Properties of Compounds of Cobalt.—Cobalt, in its salts, behaves both as a trivalent and a divalent element, although the trivalent salts are unstable except in the case of double salts. The colour of cobalt salts varies greatly according to the degree of hydration, but it is usually pink or blue. Cobalt salts absorb nitric oxide, and with ammonia readily yield complex ammino derivatives.

Pure cobalt salts free from nickel may be obtained from the impure derivatives by any of the methods described on pp. 28–4.

COBALT AND THE HALOGENS

Cobaltous Fluoride, CoF$_3$, may be obtained in the anhydrous condition as follows: on heating to fusion the chloride with excess of ammonium fluoride, the double fluoride, CoF$_2$.2NH$_4$F, is obtained; on further heating to redness in an atmosphere of an inert gas, the ammonium fluoride is volatilised, leaving amorphous cobalt fluoride which may be rendered crystalline by heating in gaseous hydrogen fluoride. Prepared in this manner the salt is formed in rose-coloured prisms, slightly soluble in water, and of density 4.43.

It fuses when heated in gaseous hydrogen fluoride to 1200–1300° C. to a ruby-red mass, and sublimes with difficulty at 1400° C. When heated with potassium hydrogen fluoride, KHF$_2$, a double salt, CoF$_3$.KF, is obtained in garnet-red crystalline plates of density 3.22.

Hydrated Cobaltous Fluoride, CoF$_3$.2H$_2$O, is easily prepared as rose-red crystals by evaporation of a solution of the oxide or carbonate in aqueous hydrogen fluoride. Boiling water decomposes the salt, yielding an insoluble oxy-fluoride of light red colour.

A crystalline hydrated acid salt, CoF$_3$.6H$_2$O.5HF, isomorphous with the corresponding nickel salt, has been described. The double salts, CoF$_3$.KF.H$_2$O and CoF$_3$.NaF.H$_2$O, have been prepared. By warming on the water-bath a solution of ammonium fluoride with cobalt oxide or hydroxide, the double ammonium cobalt fluoride, CoF$_3$.2NH$_4$F.2H$_2$O, is obtained, isomorphous with the corresponding nickel, zinc, and copper salts of general formula RF$_2$.2NH$_4$F.2H$_2$O, where R stands for a divalent metal.

Cobaltic Fluoride, CoF$_3$, may be prepared by electrolysis a saturated solution of cobaltous fluoride in 40 per cent. hydrofluoric acid contained in a platinum dish which serves as anode. the cathode being a platinum wire. It is deposited as a green powder which does not redissolve on stopping the current. In air it slowly turns grey, then red. Water readily decomposes it, yielding cobaltic hydroxide. The salt dissolves in concentrated sulphuric acid, giving a brown solution which becomes green on dilution, and red when gently warmed.

---

2 Poulenc, Compt. rend., 1892, 114, 1426.
3 Compare nickel fluoride, p. 110.
4 Poulenc, Compt. rend., 1892, 114, 746.
7 Barbieri and Calzolari, Atti R. Accad. Lincei, 1905, [v], 14, [i], 464.
Cobaltous Chloride, CoCl₂, results in the anhydrous condition when metallic cobalt or its sulphide is heated in chlorine; by heating the hydrated salt 2 to 140° C., or by calcination of the chloropentammine chloride, [CoCl₅NH₃]Cl₂, in either case in a current of hydrogen chloride; by distilling a solution of the hexahydrated chloride in anhydrous ethylene glycol under reduced pressure; and finally by treatment of a solution of the hydrated chloride with gaseous hydrogen chloride.

By the first of these methods blue crystalline scales are obtained which admit of purification by sublimation in a current of chlorine or carbon dioxide. Density, 2.937.

At red heat moist hydrogen reduces it to metallic cobalt. Dry hydrogen acts less readily, and a portion of the chloride sublimes.

Magnesium likewise reduces it at high temperatures.

The salt dissolves in alcohol to a blue solution, which becomes violet and later rose-coloured upon addition of water. Upon exposure to moist air, the anhydrous salt takes up water, forming first the dihydrate and then the tetrahydrate.

Aqueous solutions of cobalt chloride may be obtained by dissolving the anhydrous salt in water, or the oxides or carbonate in hydrochloric acid. Upon concentration in the warm the hexahydrate, CoCl₂.6H₂O, is obtained as dark red monoclinic prisms of density 1.84. These melt at 60° C. in their own water of crystallisation. They lose four molecules of water either when warmed to 50° C. over sulphuric acid, or when kept for a prolonged period in vacuo over the same, the resulting dihydrate, CoCl₂.2H₂O, being rose-coloured. The dihydrate is also obtained by precipitation from solution on addition of concentrated hydrochloric acid.

By raising the temperature to 100° C. one further molecule of water is expelled, a violet monohydrate, CoCl₂.6H₂O, remaining. The monohydrate may also be prepared by concentrating a solution of the hexahydrate in absolute alcohol at 95° C. The salt crystallises out in pale violet needles. At 110° to 120° C. the anhydrous salt is obtained as a blue mass.

The tetrahydrate, CoCl₂.4H₂O, is obtained by allowing either the anhydrous salt or the dihydrate to remain exposed to moist air. Further exposure yields the hexahydrate.

The solubility of cobalt chloride in water is as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Grams of CoCl₂ per 100 grams solution</th>
<th>Grams of CoCl₂ per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4</td>
<td>28.0</td>
<td>41.7</td>
</tr>
<tr>
<td>+7</td>
<td>31.2</td>
<td>46.7</td>
</tr>
<tr>
<td>11</td>
<td>31.3</td>
<td>48.4</td>
</tr>
<tr>
<td>12</td>
<td>32.5</td>
<td>48.8</td>
</tr>
<tr>
<td>25</td>
<td>34.4</td>
<td>50.5</td>
</tr>
<tr>
<td>34</td>
<td>37.5</td>
<td>51.2</td>
</tr>
<tr>
<td>41</td>
<td>39.8</td>
<td>52.8</td>
</tr>
</tbody>
</table>

5. Rieth, Ber., 1870, 3, 670.
In the cold the saturated solution is rose-coloured, like the crystalline hexahydrated salt. On warming it becomes violet between 25° and 50° C., above which latter temperature it is blue. This is explained by some as due to a change in hydration of the cobalt salt in solution from the red hexahydrate, through the violet monohydrate, to the blue anhydrous salt. Certainly the changes in colour correspond to breaks in the solubility curve as shown in Fig. 1. A similar change in colour from red to blue likewise occurs with increase of concentration of the solution.

![Fig. 1.—The solubility curves of cobalt chloride and iodide.](image)

This simple hydration theory cannot explain all the known phenomena, as, for example, the opposite effects of calcium chloride and zinc chloride on the colours. Engel\(^1\) therefore assumed that the observed colours were due to certain double salts present in the solutions. In the case of pure cobalt chloride, hydrolysis was supposed to occur on heating the solution, the hydrochloric acid liberated uniting with unchanged cobalt chloride; and as an explanation of the colour change this is almost certainly incorrect. Ostwald\(^3\) suggested a simple ionic explanation, namely, that the red colour is that of the cobalt cation, and the blue that of the undissociated salt. This is certainly not a complete explanation, and seems to necessitate a very marked decrease in ionisation with rise of temperature, which experiment, so far, does not support.\(^4\)

Donnan and Bassett\(^5\) suggest that cobalt chloride solution, in

---


5 Donnan and Bassett, *loc. cit.*
addition to simple ions $\text{Co}^{+}$ and $\text{Cl}^-$, contains complex anions $\text{CoCl}_2^-$ or $\text{CoCl}_4^-$, there being two equilibrium reactions in solution, as follow:

\[(a) \quad \text{CoCl}_2 \rightleftharpoons \text{Co}^{2+} + 2\text{Cl}^- \]
\[(b) \quad \text{CoCl}_2 + 2\text{Cl}^- \rightleftharpoons \text{CoCl}_4^-, \text{or} \quad \text{CoCl}_2 + \text{Cl}^- \rightleftharpoons \text{CoCl}_3^- \]

Granting that the cobalt ion in solution is red, and that the complete anion is blue and increases in concentration with rise of temperature, the observed colour changes are readily explained qualitatively; for the complex ions will break down with dilution, and also if there be added the chloride of a metal with a greater tendency to form complex ions, e.g. zinc chloride, while the formation of the complex ions $\text{CoCl}_4^-$ (or $\text{CoCl}_3^-$) will be augmented by increasing the concentration of chlorine ions, i.e. by adding hydrochloric acid or the highly dissociated chloride of a metal like calcium, which has little or no tendency to form complex ions. Donnan and Bassett found by electrolytic experiments that the blue solutions contain a blue anion and the red solutions a red cation, and further supported their view by other physico-chemical data; Denham\(^1\) has furnished additional corroborative evidence. Donnan and Bassett conclude that when the cobalt atom is in close association with chlorine, e.g. in $\text{CoCl}_2$ and $\text{CoCl}_3^-$ or $\text{CoCl}_4^-$, a blue colour is developed, but that when, by dissociation or the presence of water molecules this close association is broken, e.g. in $\text{Co}^{+}$ and $\text{CoCl}_2\cdot6\text{H}_2\text{O}$,\(^2\) a red colour is observed.

The work of Vaillant\(^3\) and Lewis\(^4\) has shown that the colour changes cannot be quantitatively interpreted without considering that water plays a definite rôle in the reactions. It follows that if Donnan and Bassett's views on complex ion formation be correct, water is either produced or used up when cobalt chloride and chloride ion interact; thus, for example, where the ion $\text{CoCl}_3^-$ is assumed for simplicity:

$$\text{CoCl}_2\cdot.n\text{H}_2\text{O} + \text{Cl}^-\cdot.m\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_3^-\cdot.p\text{H}_2\text{O} + (n + m - p)\text{H}_2\text{O}.$$ 

Kotschubei\(^5\) has determined the extent of the hydration of the cobalt ion in cobalt chloride solution by the electrolytic method briefly indicated in the first volume of this Series,\(^6\) and finds that the hydration increases with the dilution. He concludes from his own and other workers' experiments that the hydration diminishes with rise of temperature; also that the hydration of the cobalt chloride molecule varies in the same manner as that of the cobalt ion. He doubts the existence of complex ions in solutions of cobalt chloride, and considers that in the blue solutions formed by the addition of hydrochloric acid, calcium chloride, etc., the evidence for the existence of complex ions is inconclusive. On the other hand, he admits the presence of complex

---

2 These authors apply Werner's Theory to deduce that the close association is here broken.
ion in the red solutions containing mercuric chloride, etc., and formulates the ions as probably being:

\[
\left[ \text{CoCl}_4^{\text{ZnCl}_2} \right]^-, \left[ \text{CoCl}_4^{\text{HgCl}_2} \right]^-, \text{etc.}
\]

Cobalt chloride dissolves in alcohol to a blue solution, which becomes violet and then red on the addition of water. The alcoholic solution becomes red when very diluted or when cooled much below 0° C. The blue colour in these solutions has been attributed to the formation of double compound by Engel, to complex ion formation by Donnan and Bassett, and to both these causes by Kotschubei.

The change in colour undergone by cobalt chloride on varying the temperature is taken advantage of in the preparation of sympathetic inks.

The molecular weight of cobalt chloride as determined by the freezing-point method, with urethane as solvent, corresponds to the double formula, CoCl, (compare ferrous chloride), but the results obtained by the boiling-point method indicate that under those conditions the molecule is single, namely, CoCl2.

The hexammoniate, CoCl2.6NH3, is produced by passing ammonia into a concentrated aqueous solution of cobalt chloride in the entire absence of air, or by passing it into a saturated solution of cobalt chloride in methyl acetate. It yields dark rose-red octahedral crystals.

**Double Salts.**—An unstable acid chloride, CoCl2.HCl.3H2O, is obtained as blue crystals by cooling to —23° C. A saturated solution of cobalt chloride in aqueous hydrogen chloride yields dark rose-red octahedral crystals. CoCl2.LiCl.3H2O and CoCl2.NH4Cl.6H2O have also been obtained. A blue alcoholate, CoCl2.2CH3OH, is known. With iodine trichloride the complex, CoCl2.2ICl3.8H2O, is formed as orange-red crystals.

**Cobaltic Chloride,** CoCl2, has not as yet been isolated, although indications of its possible existence are not entirely wanting. Thus, when freshly precipitated hydrated cobaltic oxide is dissolved in alcoholic hydrogen chloride, a dark green solution is produced which rapidly turns to a rose colour. The first dark colour suggests the presence of trivalent cobalt.

**Cobaltous Bromide,** CoBr2, may be obtained as a green mass by passing bromine vapour or a mixture of bromine and hydrogen bromide over heated cobalt; by heating the hydrated salt to 180° C.; and also by addition of the calculated quantity of dry bromine to finely divided cobalt under ether. The green salt, CoBr2.(C2H5)2O, is produced which, on heating, yields CoBr2. The salt may be purified by sublimation in a current of hydrogen bromide. The product is
green, crystalline, of density 4·91. It begins to be reduced by dry hydrogen at about 850° C. The reaction is more rapid at higher temperatures, but is accompanied by partial sublimation. With moist hydrogen the reduction begins at 250° C.

The salt deliquesces to a dark red liquid upon exposure to air.

The solution, which also results when metallic cobalt is exposed to the prolonged action of bromine and water, yields, on concentration over sulphuric acid, splendid purple-red prismatic crystals of the hexahydrate, CoBr₂·6H₂O. These melt at 47-48° C. At 100° C. they fuse to a deep blue liquid, evolving water, and leaving on cooling purplish blue crystals of the dihydrate, CoBr₂·2H₂O. When heated to 180° C., the salt dries up to an opaque, amorphous, vivid green mass of anhydrous bromide.²

In addition to the foregoing, several other hydrates are known, their formulae and appearance, together with those above cited, being as follow ³:

<table>
<thead>
<tr>
<th>Formula</th>
<th>Appearance</th>
<th>CoBr₂·6H₂O</th>
<th>CoBr₂·2H₂O</th>
<th>CoBr₂·5H₂O</th>
<th>CoBr₂·4H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>m.pt. 47-48° C.</td>
<td>purple</td>
<td>pink</td>
<td>reddish-violet</td>
</tr>
<tr>
<td>CoBr₂·5·5H₂O</td>
<td>rose-coloured</td>
<td></td>
<td>CoBr₂·H₂O</td>
<td>CoBr₂·0·5H₂O</td>
<td>m.pt. 70-71° C.</td>
</tr>
<tr>
<td>CoBr₂·5H₂O</td>
<td>pink</td>
<td></td>
<td>CoBr₂·0·5H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoBr₂·4H₂O</td>
<td>reddish-violet</td>
<td></td>
<td>CoBr₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On exposing the anhydrous salt to ammonia gas, as also by passing ammonia into a solution of cobalt bromide in methyl acetate, the hexammoniate, CoBr₂·6NH₃, is obtained as pale rose-red crystals. These lose ammonia on heating, becoming light blue at 120° C. and having the composition CoBr₂·2NH₃.

The solubility of cobalt bromide in water is as follows ⁴:

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>59</th>
<th>75</th>
<th>97</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams CoBr₂ in 100 grams solution</td>
<td>66·7</td>
<td>66·8</td>
<td>68·1</td>
</tr>
</tbody>
</table>

When dissolved in organic liquids the molecular weight, as determined by ebullioscopic methods, appears to correspond to the single formula, CoBr₂.⁵

**Cobaltous Iodide**, CoI₂, may be obtained in the anhydrous condition by heating cobalt in a current of iodine vapour, or by desiccation of the hydrated salt over concentrated sulphuric acid in vacuo.⁶ It is then obtained as a black metallic-looking mass. It dissolves in water, yielding interesting colour changes possessing in concentrated solution a green colour, which become brown and finally red on dilution.⁷

Cobalt iodide is most readily obtained in solution by warming the finely divided metal with water and iodine. Its formation is accompanied by evolution of heat. It may also be obtained by allowing cobalt to remain in prolonged contact with water and iodine.²

2 Hartley, loc. cit.
Several hydrates have been isolated. The *hexahydrate*, $\text{CoI}_2.6\text{H}_2\text{O}$, is obtained by slightly evaporating and then strongly cooling the aqueous solution. It yields dark red, hexagonal prisms. Further concentration yields the *nonahydrate*, $\text{CoI}_2.9\text{H}_2\text{O}$, which crystallises in thin, red, rhombic plates, which lose three molecules of water at $64^\circ$ C.¹ The *tetrahydrate*, $\text{CoI}_2.4\text{H}_2\text{O}$, and *dihydrate*, $\text{CoI}_2.2\text{H}_2\text{O}$, are green.

The solubility of cobalt iodide in water is as follows²:

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>Grams of CoI₂ per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>Grams of CoI₂ per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>46</td>
</tr>
</tbody>
</table>

The solution changes in colour as the temperature rises, being red below $20^\circ$ C., olive between $20^\circ$ and $40^\circ$ C., and green at higher temperatures. These changes correspond to breaks in the solubility curve, as shown in Fig. 2, and are usually regarded as indicating the existence in solution of the hexa-, tetra-, and di-hydrates respectively. Both the *hexammoniate*, $\text{CoI}_2.6\text{NH}_3$, and *tetrammoniate*, $\text{CoI}_2.4\text{NH}_3$, have been prepared.³

*Double Salts* of cobalt iodide are known.⁴

**OXY-HALOGEN DERIVATIVES OF COBALT**

*Cobalt Oxy-fluoride*, $\text{CoF}_2.\text{CoO}.\text{H}_2\text{O}$, is obtained by decomposing hydrated cobalt fluoride with boiling water, or by addition of excess of cobalt carbonate to aqueous hydrogen fluoride.⁵ It is a rose-coloured, crystalline powder.

---

**Cobalt Oxy-chloride** is obtained as a blue precipitate turning red on pouring a hot solution of cobalt chloride into dilute ammonium hydroxide. The formula CoCl₂.3CoO.3·5H₂O, has been attributed to it. Another basic salt, CoCl₂·2Co(OH)₂·5H₂O, is stated to result as a precipitate by the action of calcium carbonate upon aqueous solutions of cobalt chloride.

**Cobalt Chlorate**, Co(ClO₃)₂, may be obtained by double decomposition of solutions of cobalt sulphate and barium chlorate. The solution, when concentrated by exposure to sulphuric acid at temperatures below 18° C., yields unstable dull red rhomboic crystals of the *hexahydrate*, Co(ClO₃)₂·6H₂O. These melt at about 18·5° C. with separation of the *tetrahydrate*, Co(ClO₃)₂·4H₂O, which is fairly stable at low temperatures, but becomes less so as the temperature rises up to about 61° C., at which point dehydration takes place. Even below this temperature a certain amount of decomposition takes place, with evolution of chlorine and oxygen, an oxide of cobalt being simultaneously produced. A bright red *dihydrate*, Co(ClO₃)₂·2H₂O, may be obtained by prolonged exposure of the tetrahydrate to the action of phosphorus pentoxide.

The solubility of cobalt chlorate in water is as follows:

<table>
<thead>
<tr>
<th>Temperature ° C.</th>
<th>0</th>
<th>10·5</th>
<th>18</th>
<th>21</th>
<th>35</th>
<th>47</th>
<th>61</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams of Co(ClO₃)₂ per 100 grams solution</td>
<td>57·45</td>
<td>61·83</td>
<td>64</td>
<td>64·39</td>
<td>67·09</td>
<td>69·66</td>
<td>76·12</td>
</tr>
</tbody>
</table>

**Cobalt Perchlorate**, Co(ClO₄)₂, 5H₂O, may be obtained by dissolving cobalt carbonate or hydroxide in a solution of perchloric acid, expelling the excess of acid at 110° C., and concentrating to crystallisation. The salt separates out in long red needles which are very soluble in water, alcohol, and acetone, but are insoluble in chloroform. When dried over sulphuric acid the crystals contain five molecules of water, and melt at 143° C. They are more stable than the corresponding pentahydrate of nickel perchlorate, and do not decompose at 103° C., neither does their aqueous solution undergo hydrolytic decomposition.

The solubility of cobalt perchlorate in water is as follows:

<table>
<thead>
<tr>
<th>Temperature ° C.</th>
<th>30·7</th>
<th>21·3</th>
<th>0</th>
<th>7·5</th>
<th>18</th>
<th>26</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Co(ClO₄)₂ in 100 grams solution</td>
<td>19·02</td>
<td>20·72</td>
<td>22·90</td>
<td>23·35</td>
<td>23·75</td>
<td>25·95</td>
<td>26·33</td>
</tr>
</tbody>
</table>

Density of solution — — 1·5639 1·5658 1·5670 1·5811 1·5873

At — 21·8° C. the *nonahydrate*, Co(ClO₄)₂·9H₂O, is formed. The *hexahydrate*, Co(ClO₄)₂·6H₂O, is described by Salvadori as crystallising in hexagonal prisms, which are pale pink in colour and show feeble polychroism. Heated to 100° C. the salt loses water, yielding a violet, hygroscopic powder. When rapidly heated it deflagrates without explosion, but it explodes on percussion.

When ammonia and ammonium perchlorate are added to an aqueous solution of calcium perchlorate, the *hexammoniate*, Co(ClO₄)₂·6NH₃, is

---

5 Meusser, *ibid.*, 1902, 35, 1418.
7 Salvadori, *Gazzetta*, 1912, 42, [i], 458; 1910, 40, [ii], 9.
formed as a red precipitate. Boiling water effects its decomposition according to the equation:

$$2\text{Co(ClO}_4\text{)}_2\cdot 6\text{NH}_3 + 2\text{H}_2\text{O} = \text{Co(OH)}_2 + \text{Co(ClO}_4\text{)}_2 + 2\text{NH}_4\text{ClO}_4 + \text{NH}_3.$$  

The anhydrous salt, $\text{Co(ClO}_4\text{)}_2$, cannot be isolated since the hydrated salt decomposes before all the water has been expelled.

**Cobalt Bromate**, $\text{Co(BrO}_3\text{)}_2\cdot 6\text{H}_2\text{O}$, is obtained by double decomposition of barium bromate with cobalt sulphate. On concentrating the filtered solution the salt crystallises out in red, octahedral crystals, which are readily decomposed by heat.\(^\text{1}\)

**Cobalt Iodate**, $\text{Co(IO}_3\text{)}_2$, was known to Rammelsberg\(^\text{2}\) in 1838, and was further studied by Fullerton\(^\text{3}\) and Ditte,\(^\text{4}\) the last-named investigator claiming to have prepared the anhydrous salt, and salts with 2, 3, 4, and 5 molecules of water, whilst Fullerton describes a hexahydrate.

Meusser\(^\text{5}\) confirms the existence of the anhydrous salt, and of the di- and tetra-hydrates, but throws doubt on the existence of the tri-, penta-, and hexa-hydrates.

The anhydrous salt may be obtained by maintaining for a prolonged period at 80° to 90° C. a mixed solution of cobalt nitrate and alkali iodate in the presence of free nitric acid. It is also formed at ordinary temperatures by mixing saturated solutions of cobalt nitrate and alkali iodate and agitating with a glass rod the flocculent, rose-coloured, hydrated precipitate, when it yields the blue-violet anhydrous compound. The salt is also produced by heating the same solutions from two to three hours in a glass tube at 120° C.

Anhydrous cobalt iodate yields microscopic needles, blue-violet in colour, and which on heating become dark blue in colour, but regain their original hue on cooling. Below 200° C. decomposition sets in, iodine and oxygen being evolved.

The **dihydrate**, $\text{Co(IO}_3\text{)}_2\cdot 2\text{H}_2\text{O}$, is obtained by mixing equivalent amounts of cobalt nitrate and alkali iodate (or free iodic acid) in ten times their weight of water and allowing to crystallise at 30° C. Microscopic crystals of lilac hue are obtained, which are the stable form of the salt up to 68° C.

The **tetrahydrate**, $\text{Co(IO}_3\text{)}_2\cdot 4\text{H}_2\text{O}$, is obtained as red crystals by evaporating a 5 per cent. solution containing equivalent proportions of cobalt nitrate and iodic acid at 0° to 20° C. When agitated for a prolonged period with water at 30° C. the tetrahydrate yields the dihydrate.

The various solubilities of the hydrates of cobalt iodate at different temperatures are as follow\(^\text{5}\):

| Tetrahydrate, $\text{Co(IO}_3\text{)}_2\cdot 4\text{H}_2\text{O}$ |
|-----------------|---|---|---|---|---|
| Temperature ° C. | 0 | 18 | 30 | 50 | 60 | 65 |
| Grams $\text{Co(IO}_3\text{)}_2$ per 100 grams solution | 0.54 | 0.83 | 1.03 | 1.46 | 1.86 | 2.17 |

\(^{2}\) Rammelsberg, *ibid.*, 1838, 44, 562.  
\(^{5}\) Meusser, *Ber.*, 1901, 34, 2432.
**Dihydrate, Co(IO₃)₂·2H₂O**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>18</th>
<th>30</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Co(IO₃)₂ per 100 grams solution</td>
<td>0.82</td>
<td>0.45</td>
<td>0.52</td>
<td>0.67</td>
<td>0.84</td>
<td>1.02</td>
</tr>
</tbody>
</table>

**Anhydrous Salt, Co(IO₃)₂**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>18</th>
<th>30</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Co(IO₃)₂ per 100 grams solution</td>
<td>1.03</td>
<td>0.89</td>
<td>0.85</td>
<td>0.75</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

These results are shown graphically in Fig. 3, and are interesting as showing the rapid rise in solubility of the tetrahydrate with increase of temperature, and the simultaneous fall in solubility of the anhydrous salt.

**Cobalt Periodate** is unknown, but a basic substance corresponding to the formula 7CoO·2I₂O₆·18H₂O is obtained on concentrating mixed solutions of sodium periodate and cobalt sulphate. It is a yellowish green powder.¹

---

**COBALT AND OXYGEN**

Cobalt, like iron, combines with oxygen to form three well-defined oxides, namely, cobaltous oxide, CoO; cobaltic oxide, Co₂O₃; and cobalto-cobaltic oxide, Co₃O₄. In addition to these, a peroxide, CoO₂, appears capable of existing, whilst numerous other complex bodies have been described, such as Co₅O₉,² Co⁴O₅,³ Co₆O₇,⁴ Co₇O₁₁,⁵ and Co₈O₉.⁶ Probably, however, these are not separate chemical entities, but mixtures of the simpler oxides as in the case of analogous complex oxides of iron.⁷

---

Cobaltous Oxide, Cobalt Monoxide, CoO, may be obtained from cobaltic oxide by reduction in a current of ammonia, or of hydrogen at about 350° C. At higher temperatures metallic cobalt is obtained.

Cobaltous oxide also results when cobaltic oxide or cobalt carbonate is heated to redness in carbon dioxide or nitrogen; when cobalt is heated in nitric oxide to 150° C.; and when cobalt sulphate is heated to whiteness.

Obtained by any of the foregoing methods cobaltous oxide is a stable powder, greyish in colour, which on heating in air takes up oxygen forming cobalto-cobaltic oxide. Its density is about 5·68 when obtained by calcination from a higher oxide. Prepared from the sulphate it retains the crystalline form of the latter, and its density is 6·70. It is reduced to metallic cobalt when heated in carbon monoxide at temperatures above 450° C., or in hydrogen above 250° C. An allotropic modification of cobaltous oxide is formed by heating cobalto-cobaltic oxide with 2 to 3 per cent. of carbon at about 900° C. It is yellowish green in colour.

Neither allotrope is magnetic.

When heated gently in air it yields tri-cobalt tetroxide, Co₃O₄. In hydrogen sulphide the oxysulphide CoO·CoS is produced.

It unites with acids to form cobaltous salts. It replaces ammonia in its salts and is dissolved by potassium hydroxide, yielding a deep blue solution.

Cobalt oxide unites with or forms solid solutions with many other metallic oxides at high temperatures. Thus, with alumina at 1100° C. a blue aluminate, Co₅O₆Al₂O₃, is formed, whilst at higher temperatures a green compound, 4CoO·8Al₂O₃, is produced. With stannic oxide, cobalt oxide yields a dark green ortho-stannate, 2CoO·SnO₂, or Co₂SnO₄. The same compound is produced by precipitating cobalt metastannate from a solution of a cobalt salt by addition of potassium metastannate, and heating the precipitate. The colour is then greenish blue, the blue tinge resulting from the excess of stannic oxide. With chromic oxide a green chromite, CoO·Cr₂O₃, is obtained; the vanadate and tantalate are likewise green, whilst the uranate is yellow.

Cobalt Blue consists essentially of oxides of cobalt and aluminium with more or less zinc oxide. It is obtained by calcining a mixture of alum and cobalt sulphate, and is used by artists in painting porcelain. Save for this it has now no commercial value. Cobalt blue is also known as Cobalt Ultramarine, Thenard’s Blue, and King’s Blue.

Cobalt Green or Rinmann’s Green was discovered in the eighteenth century by a Swede named Rinmann, who obtained it by heating
a mixture of zinc oxide and cobalt oxide. It can be obtained in a variety of other ways. Large crystals may be prepared by heating zinc oxide with cobalt carbonate at 1100\degree\text{C}, potassium chloride being used as a flux. The product is cooled in carbon dioxide when thin tabular crystals are usually obtained, green in colour, and of density 5·69. Analysis indicates a composition corresponding to CoO\cdot4·8ZnO. It is not a definite chemical entity, but a solid solution of the two oxides in one another.\footnote{Hedvall, Ber., 1912, 45, 2095; Arkiv. Kem. Min. Geol., 1913, 5, No. 6, 1; 1914, 5, No. 18, 1.} \textbf{Turquoise Green} is similar, but contains some oxide of chromium in addition. Both pigments are used in porcelain painting. \textbf{Cobalt Red} is obtained in a similar manner to Rinmann’s green, save that the zinc oxide in the latter is replaced by magnesium oxide.\footnote{See Hedvall, Zeitsch. anorg. Chem., 1914, 86, 296.}

\textbf{Cobaltous Hydroxide}, Co(OH)$_2$—When potassium hydroxide is added to an aqueous solution of a cobaltous salt, carefully freed from air, a blue precipitate is obtained which, on heating, is converted into the rose-coloured hydroxide.

The blue precipitate was at one time regarded as a basic salt, but Hantzsch\footnote{Hantzsch, Zeitsch. anorg. Chem., 1912, 73, 304.} showed that any basic salt can be washed out without impairing the colour of the mass. It may be completely dehydrated at 170\degree\text{C}, whereas the pink hydroxide retains some water even after prolonged exposure to 300\degree\text{C.} in an atmosphere of nitrogen. The formula suggested for the blue compound is, accordingly, CoO\cdot H$_2$O, and for the pink one, Co(OH)$_2$.

Cobalt hydroxide dissolves in ordinary distilled water to the extent of 3·18 mgs. of Co(OH)$_2$ per litre at 20\degree\text{C.}\footnote{Almkvist, Zeitsch. anorg. Chem., 1918, 103, 240.}

Like its ferrous analogue, cobalt hydroxide readily absorbs oxygen, yielding a brown mass. When dissolved in acids stable cobaltous salts are obtained, but when dissolved in hot, concentrated aqueous potassium hydroxide and allowed to cool, cobaltous oxide gradually crystallises in microscopic prisms\footnote{De Schulten, Compt. rend., 1889, 109, 266.} which are deposited as a violet powder. The crystals are pleochroic, of density 3·597 at 15\degree\text{C.}, permanent in air and insoluble in ammonium hydroxide. They are soluble in acetic acid, in sodium hydroxide, and in hot solutions of ammonium chloride.

\textbf{Cobalto-cobaltic Oxide, Tri-cobalt Tetroxide}, Co$_3$O$_4$, is the essential constituent of commercial oxide of cobalt. It is produced when either of the other oxides is strongly heated in air, and when cobalt nitrate is ignited.

It is a black, hygroscopic powder, of density 5·8 to 6·8.\footnote{Rammelsberg, Pogg. Annalen, 1849, 78, 93; Zimmermann, Annalen, 1886, 232, 324.} It dissolves in hydrochloric acid, evolving chlorine.

A crystalline form of this oxide results when cobalt chloride or a mixture of this and ammonium chloride is heated in air or oxygen, microscopic octahedra possessed of metallic lustre being obtained.\footnote{Schwarzenberg, Annalen, 1856, 97, 212; Gorgeu, Compt. rend., 1885, 100, 175; Gibbs and Gentz, Amer. J. Sci., 1857, 23, 234, 319; 24, 86.}

The oxide differs from its iron analogue in not being magnetic. When strongly heated in the oxyhydrogen flame it yields metallic cobalt, which, as it cools, becomes tarnished with a film of oxide.\footnote{Read, Trans. Chem. Soc., 1894, 65, 314.}
various actions of hydrogen, carbon monoxide, and aluminium upon
this oxide have already been discussed (see pp. 24–25).

Cobaltic oxide has been prepared in three states of hydration. The trihydrate, \( \text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \), results on warming cobaltous hydroxide with potassium persulphate and heating the resulting product to 100° C. with dilute nitric acid.\(^1\) It is also produced as a brown precipitate on boiling a solution of roseo-cobaltic sulphate.

The hexahydrate, \( \text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \), occurs as a green precipitate on adding baryta water to a cold solution of cobalt chloride in vacuo.\(^2\)

The heptahydrate, \( \text{Co}_2\text{O}_3 \cdot 7\text{H}_2\text{O} \), results after exposing for several months in a vacuum desiccator the brown precipitate obtained by allowing cobaltous hydroxide to remain in contact with air.\(^3\)

Cobalt Sesquioxide, \( \text{Co}_3\text{O}_4 \), results when cobalt nitrate is gently heated to 180° C.\(^4\) It is a black, amorphous powder, of density 5.18. Hydrogen begins to reduce it at 182° C.\(^5\) It may be regarded as the cobalt salt of cobaltous acid, namely, cobaltous cobaltite, \( \text{CoCo}_2\text{O}_4 \).

Hydrated Cobaltic Oxide, \( \text{Co(OH)}_2 \) or \( \text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \), is obtained in a more or less complete state of hydration when an alkaline oxidiser,\(^6\) such as, for example, an alkaline solution of ammonium persulphate,\(^7\) or of sodium hypochlorite,\(^8\) is added to a cobalt salt. The precipitate varies in composition according to the conditions obtaining at the moment. When an alkaline solution of cobalt sulphate is electrolysed the oxide is obtained in at least two stages of hydration, namely, the dihydrate, \( \text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \), and the trihydrate, \( \text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \).\(^9\)

As obtained by the foregoing methods, hydrated cobaltic oxide is a blackish brown precipitate which dissolves in aqueous hydrogen chloride evolving chlorine, cobaltous chloride passing into solution. The oxide thus behaves like a peroxide.

With well-cooled acids, brownish solutions are obtained which are presumed to contain cobaltic salts.

The oxide always contains traces of alkali. At 335° C. it becomes anhydrous, but loses a little oxygen, a small quantity of \( \text{Co}_2\text{O}_3 \) being formed.\(^10\) Hydrogen begins to reduce it at 110° C., carbon at 260° C., and carbon monoxide at −11° C.\(^11\)

Cobalt Dioxide, Cobalt Peroxide, \( \text{CoO}_2 \), is obtained in the hydrated condition as a greenish black precipitate by treating aqueous solutions of cobaltous salts with iodine and sodium hydroxide.\(^12\) It is also obtained by acting on a cobaltous salt with a hypochlorite.\(^13\) It decomposes at 100° C., and when washed undergoes partial reduction.

\(^1\) Mawrow, Zeitsch. anorg. Chim., 1900, 24, 263.
\(^7\) Mawrow, Zeitsch. anorg. Chem., 1900, 24, 263; Hüttner, ibid., 1901, 27, 81.
\(^11\) Wright and Luff, ibid., 1878, 33, 535.
\(^12\) Vortmann, Ber., 1891, 24, 2744; Hüttner, Zeitsch. anorg. Chem., 1901, 27, 81; Metz, ibid., 1914, 86, 358.
\(^13\) McLeod, Brit. Assoc. Reports, 1892, p. 669.
McConnell and Hanes \(^1\) claim to have obtained the monohydrate or cobaltous acid, \(H_2CoO_3\), by the action of hydrogen peroxide upon cobaltous hydroxide in aqueous suspension.\(^2\) If the acid can exist at all in the free state it is very unstable, although some of its salts are well defined.

The more important cobaltites are cobaltous cobaltite, \(CoCoO_3\), more usually known as cobaltic oxide, \(Co_2O_3\); and cobaltous dicobaltite, \(Co_2.2CoO_2.2H_2O\), which has been obtained \(^3\) as glistening hexagonal plates by fusion of cobaltous oxide with potassium peroxide and washing with water. Bayley \(^4\) had already indicated the existence of this substance in 1879, and believed that at least two other hydrates exist, namely, \(CoO.2CoO_2.4H_2O\) and \(CoO.2CoO_2.3H_2O\), and possibly the monohydrate, \(CoO.2CoO_2.3H_2O\).

Magneisium cobaltite, \(MgO.C_2O_2\); barium cobaltite, \(BaO.C_2O_2\), and dicobaltite, \(BaO.2CoO_2\), \(^6\) and a potassium cobaltous cobaltite, \(K_2O.C_3O_2\), \(^7\) have also been described.

### COBALT AND SULPHUR

**Cobalt Monosulphide, Cobaltous Sulphide**, \(CoS\), occurs in nature as the mineral syepoorite or jaipurite. The mineral has been prepared artificially by fusing cobalt sulphate with barium sulphide and sodium chloride.\(^8\) The monosulphide is also obtained by heating a solution of cobalt sulphite \(^9\) to \(200^\circ\) C., or a mixture of solutions of cobalt salts with ammonium thiocyanate to \(180^\circ\) C., in either case in sealed tubes,\(^10\) and by heating cobalt sulphate and carbon to the temperature of the electric arc.\(^11\)

By the first of these methods cobalt monosulphide is obtained as steel-grey, elongated prisms of density \(5.45\). The remaining processes yield the amorphous substance. Prolonged contact with air and water effects its oxidation to the sulphate. Acids dissolve it, yielding cobaltous salts.

Cobalt monosulphide is also obtained as a black hydrated precipitate on addition of ammonium sulphide to a neutral solution of a cobalt salt. Although the precipitate is soluble only with difficulty in hydrochloric acid it is not obtained when hydrogen sulphide is passed into a solution of a cobalt salt acidified with a mineral acid. The explanation is probably similar to that given for the nickel analogue (q.v.). An OXysulphide, \(CoO.C_2O_3\), is stated to result on heating cobalt monoxide in a current of hydrogen sulphide.\(^12\)

---

\(^2\) Durrant (*ibid.*, 1905, 87, 1781) was unable to confirm this. See also Job, *Compt. rend.*, 1898, 127, 100.
\(^3\) Hofmann and Hiendlmaier, *Ber.*, 1906, 39, 3184. Nickel under similar conditions yields nickelic nickelite, \(NiO.NiO_2.2H_2O\).
\(^4\) Bayley, *Chem. News*, 1879, 39, 81; 1900, 82, 179.
\(^5\) Dufau, *Compt. rend.*, 1896, 123, 239.
\(^6\) Rousseau, *Compt. rend.*, 1889, 109, 64.
\(^8\) Hiebert, *Compt. rend.*, 1867, 65, 75.
\(^12\) Schumann, *Annalen*, 1877, 187, 313.
Tricobalt Tetrasulphide, $\text{Co}_3\text{S}_4$, has been obtained in the crystalline form by heating solutions of potassium sulphide with cobalt chloride in sealed tubes to 160–180° C.\(^1\)

Cobalt Sesquisulphide, $\text{Co}_3\text{S}_3$, results when a mixture of sulphur and the carbonates of cobalt and potassium are raised to white heat.\(^2\) Nickel, in similar circumstances, yields double sulphides such as $\text{K}_2\text{S}_8\text{NiS}$, and thus resembles palladium and platinum, whilst cobalt behaves more like rhodium and iridium. The position of cobalt before nickel in the Periodic Table is thus supported.

Cobalt Disulphide, $\text{CoS}_2$—Setterberg\(^3\) believed that this sulphide results on heating cobalt monoxide to redness, either in contact with sulphur or in a current of hydrogen sulphide. The mass is treated with dilute hydrochloric acid, leaving an unstable residue of disulphide. Moist air oxidises it to the sulphate, whilst the application of heat expels some of the sulphur.

Polysulphides.—A study of the freezing-point diagram of the cobalt sulphides suggests the possibility of the formation of the complexes $\text{Co}_3\text{S}_3$ and $\text{Co}_6\text{S}_5$.\(^4\) Hiortdahl\(^5\) claimed to have obtained the former of these by heating tricobalt tetroxide to redness in a current of hydrogen sulphide. It is doubtful, however, if it should be regarded as a separate chemical entity.

According to Chesneau,\(^6\) a polysulphide, $\text{Co}_9\text{S}_7$, is precipitated as a black mass when a solution of sulphur in aqueous sodium monosulphide is added to one of cobalt chloride. If this precipitate is dissolved in sodium polysulphide solution and the liquid evaporated in vacuo, black crystalline plates separate out.

Cobaltous Sulphide, $\text{CoSO}_3$, is obtained in the hydrated condition as rose-coloured crystals by dissolving cobaltous hydroxide in sulphurous acid and concentrating at a low temperature.\(^7\) Muspratt found the crystals to contain five molecules of water, and Rammelsberg three. Röhrig\(^8\) some years later proved that both hydrates exist. The salt is but sparingly soluble in water, yielding a readily oxidisable solution. With alkali sulphides double salts are obtained. Thus

Potassium Cobalt Sulphite, $\text{K}_2\text{SO}_3\cdot\text{CoSO}_3$, is obtained as a pale red precipitate on warming mixed solutions of a soluble cobalt salt and potassium sulphite. Ammonium Cobalt Sulphite, $(\text{NH}_4)_2\text{SO}_3\cdot\text{CoSO}_3$, is prepared in a similar manner.\(^9\) A sodium salt\(^10\) and basic sulphites have been described.\(^12\)

Cobaltic Sulphite, $\text{Co}_2(\text{SO}_3)_3$, has not been isolated, but apparently it can exist momentarily in solution. This was indicated by

2. Fellenberg, Pogg. Annalen, 1840, 53, 73; Schneider, ibid., 1874, 151, 437; Bellucci, loc. cit.
4. Friedrich, Metallurgie, 1908, 5, 212.
Meyer,\(^1\) who dissolved cobaltic hydroxide in sulphurous acid. At first a brown colour was produced, rapidly giving place to a rose-red tint which remained permanent even on boiling. The colour change is attributable to the formation of the unstable cobaltic sulphite which decomposes into cobaltous sulphite and dithionate respectively. Thus:

\[
\text{Co}_2(\text{SO}_3)_3 = \text{CoSO}_3 + \text{CoS}_2\text{O}_6.
\]

Stable double and complex cobaltic salts are known.\(^2\)

**Cobalt Thiosulphate**, \(\text{CoS}_2\text{O}_3\cdot6\text{H}_2\text{O}\), is prepared \(^3\) by mixing equivalent solutions of cobalt sulphate and strontium thiosulphate. After filtering off the insoluble strontium sulphate, the solution is concentrated over sulphuric acid, when a deliquescent, dark red crystalline mass separates out.

**Cobalt Dithionate**, \(\text{CoS}_2\text{O}_6\), may be obtained in several states of hydration. The solution is formed by double decomposition of barium dithionate and cobalt sulphate solutions. On concentration by exposure at room temperature the clear liquid, freed by filtration from insoluble barium sulphate, deposits rose-coloured, triclinic crystals of the *octahydrate*, \(\text{CoS}_2\text{O}_6\cdot8\text{H}_2\text{O}\), which are excessively soluble in water, but which effloresce in dry air. Exposed to desiccation over sulphuric acid, 2 or 4 molecules of water are lost, whilst recrystallisation from absolute alcohol yields the *hexahydrate*, \(\text{CoS}_2\text{O}_6\cdot6\text{H}_2\text{O}\), as rose-coloured prisms.\(^4\) The salt may also be obtained by dissolving cobaltic hydroxide, resulting from the combined action of bromine and caustic soda upon a solution of a cobalt salt, in sulphurous acid. At first a brown colour is produced, due to the formation of cobaltic sulphate, but this rapidly gives place to a rose-red colour, which is permanent even on boiling. This is due to decomposition of the sulphate into the sulphite and dithionate respectively:

\[
\text{Co}_2(\text{SO}_3)_3 = \text{CoSO}_3 + \text{CoS}_2\text{O}_6.\]

With concentrated aqueous ammonia the *pentammoniate*, \(\text{CoS}_2\text{O}_6\cdot5\text{NH}_3\), is obtained \(^6\) as small prisms.

**Cobalt Sulphate**, \(\text{CoSO}_4\), is obtained in the anhydrous condition by raising any of its hydrates to dull redness, or by simply maintaining the heptahydrate at 250\(^\circ\) C. until all the water has been expelled \(^7\); by evaporation of a solution of any of its hydrates in concentrated sulphuric acid \(^8\); or by heating a hydrate with ammonium sulphate.\(^9\)

By the last of these methods the salt is obtained in stable, purple-red, truncated octahedra, of density 3.65.\(^10\) With ammonia it yields the *hexammoniate*, \(\text{CoSO}_4\cdot6\text{NH}_3\).\(^11\) Heated in a tube open at both ends, anhydrous cobalt sulphate begins to decompose at 718\(^\circ\) C., yielding cobalt monoxide.\(^12\)

\(^1\) J. Meyer, *Ber.*, 1901, 34, 3606.


\(^8\) Etard, *Compt. rend.*, 1875, 87, 602.


\(^10\) Thorpe and Watte give density = 3.472; Playfair, 3.444.


Anhydrous cobalt sulphate is very stable in air at ordinary temperatures, and dissolves but slowly in hot water. The solution can be more readily prepared by dissolving the oxides or carbonate in dilute sulphuric acid. Upon evaporation at room temperatures the heptahydrate, CoSO$_4$.7H$_2$O, crystallises out. A convenient method of preparing this hydrate consists in dissolving tricobalt tetroxide in hydrochloric acid, adding an equivalent of sulphuric acid and allowing to crystallise after evaporating off the hydrogen chloride. Obtained in this manner the crystals are acidic, but may be freed from acid by precipitation from aqueous solution with alcohol and recrystallisation from pure water.

The crystals are red in colour, of density 1 1.924, and isomorphous with their iron and nickel analogues. They melt at 96° to 98° C., and effloresce upon exposure to air, losing one molecule of water. Practically insoluble in absolute alcohol, the crystals readily dissolve in methyl alcohol and in water, the solubility in the last-named solvent being as follows 4:

<table>
<thead>
<tr>
<th>Temperature ° C.</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams CoSO$_4$ in 100 grams H$_2$O</td>
<td>25.55</td>
<td>30.55</td>
<td>36.21</td>
<td>48.85</td>
<td>60.4</td>
<td>70.0</td>
<td>83.0</td>
</tr>
</tbody>
</table>

The heptahydrate is found in nature as the mineral cobalt vitriol or bieberite.

A concentrated solution of cobalt sulphate maintained at 25° C. deposits monoclinic crystals of the hexahydrate, CoSO$_4$.6H$_2$O, isomorphous with its zinc sulphate analogue. Density 2·019.5

The pentahydrate, CoSO$_4$.5H$_2$O, was stated 6 to result on exposing the heptahydrate over concentrated sulphuric acid. Density 2·134.

The tetrahydratet, CoSO$_4$.4H$_2$O, is obtained by exposing finely powdered heptahydrate to desiccation over sulphuric acid until a constant weight is arrived at.7 It is also produced by pouring the concentrated solution into sulphuric acid.8 Density 2·327.9

The trihydrate, CoSO$_4$.3H$_2$O. The existence of this hydrate has not as yet been definitely ascertained.10

The dihydrate, CoSO$_4$.2H$_2$O, is obtained by boiling the hydrate in a fine state of division in absolute alcohol.11 Density 2·712.

The monohydrate, CoSO$_4$.H$_2$O, is precipitated on adding excess of concentrated sulphuric acid to an aqueous solution of cobalt sulphate;12 by evaporation of an acid solution of the salt 13 on the sand-bath until

1 Schiff, Annalen, 1858, 108, 21. Thorpe and Watts give the density as 1.918 (loc. cit.).
2 Tilden, Trans. Chem. Soc., 1884, 45, 266.
3 De Bruyn, Zeitsch. physikal. Chem., 1892, 10, 784.
6 Playfair. See Thorpe and Watts, loc. cit.
7 Thorpe and Watts, loc. cit.
8 Moissan, Traité de Chimie Minérale, 1905, vol. iv.
9 Thorpe and Watts, loc. cit.
10 The experiment described by Vortmann (Ber., 1882, 15, 1888) is not, and is not claimed to be, conclusive.
11 Playfair, and Thorpe and Watts, loc. cit.
12 Etard, Compt. rend., 1878, 87, 602.
sulphur dioxide is evolved; and by heating the heptahydrate to 100 °C. until no further loss in weight accrues; by decomposition of purpureo-cobalt chloride in a small quantity of water with concentrated sulphuric acid until the salt has passed into solution. The whole is then heated to 220 °C. on a sand-bath. On cooling the acid is decanted, the salt washed with cold water, and finally with alcohol.

As prepared in this manner cobalt sulphate monohydrate is a red, crystalline powder, very slowly soluble in water. Exposed to moist air it slowly absorbs water. At red heat it loses water, becoming anhydrous. Density 3.125.

Basic Cobalt Sulphates.—Several of these have been described as resulting on addition of ammonia,4 cobalt carbonate5 or calcium carbonate6 to solutions of cobalt sulphate under varying conditions. The products obtained consist of blue, bluish green, and lilac precipitates of variable composition.

Double Salts.—Numerous double salts of cobalt sulphate have been prepared. Chief amongst these are salts of the type $\text{M}_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, where M stands for ammonium or an alkali metal—potassium, rubidium, or caesium. Each of these salts has been obtained and its crystallographic constants determined.7 The series is isomorphous with the corresponding ferrous and nickel double salts, and with their double selenates; the individual salts are discussed below. Other double salts are cupric cobaltous sulphate,8 $\text{CuSO}_4 \cdot 2\text{CoSO}_4 \cdot 3\text{H}_2\text{O}$, and cobaltous nickel sulphate, $(\text{Co}, \text{Ni})\text{SO}_4 \cdot \text{H}_2\text{O}$, in which the cobalt and nickel appear interchangeable.9

Ammonium Cobalt Sulphate, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, is obtained by evaporation of mixed solutions of ammonium and cobalt sulphates in equivalent proportions. The crystals are red, exhibiting pleochroism,10 and of density 1.873.11 Their solubility in water is as follows:12

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>10</th>
<th>18</th>
<th>23</th>
<th>35</th>
<th>45</th>
<th>60</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CoSO}_4$ in 100 grams of water</td>
<td>8</td>
<td>9</td>
<td>11.6</td>
<td>15.2</td>
<td>17.1</td>
<td>19.6</td>
<td>25</td>
<td>34-5</td>
</tr>
</tbody>
</table>

An anhydrous double salt, of composition $2(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{CoSO}_4$, is obtained by heating anhydrous cobalt sulphate13 with excess of ammonium sulphate. In contact with water it readily hydrates with evolution of heat.

Lithium sulphate does not appear to unite with cobalt sulphate on heating in the anhydrous condition, but sodium sulphate yields the double salt, $\text{CoSO}_4 \cdot 8\text{Na}_2\text{SO}_4$, which decomposes at 425 °C. With potassium sulphate two compounds are obtained, namely, $\text{CoSO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{CoSO}_4 \cdot 2\text{K}_2\text{SO}_4$.

1 Vortmann, Ber., 1882, 15, 1888.
2 Thorpe and Watts, loc. cit.
3 Vortmann, loc. cit.
4 Habermann, Monatsh., 1884, 5, 432.
5 Athanasseso, Compt. rend., 1886, 103, 271.
9 Scott, loc. cit.
10 Müller, Pogg. Annalen, 1855, 96, 340.
12 Tobler, Annalen, 1855, 95, 193.
which decomposes above 560° C., and 2CoSO₄.K₂SO₄, which crystallises out at 736° C.¹

**Potassium Cobalt Sulphate**, K₂SO₄·CoSO₄·6H₂O, is prepared in an analogous manner to the ammonium salt (vide supra). Its solubility in water is given as follows ²:

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>0</th>
<th>12</th>
<th>15</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>49</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams of K₂SO₄·CoSO₄ in 100 grams H₂O</td>
<td>19-1</td>
<td>30</td>
<td>32-5</td>
<td>39-4</td>
<td>51-9</td>
<td>64-6</td>
<td>81-3</td>
</tr>
</tbody>
</table>

Its density is 2-212.

**Cobaltic Sulphate**, Co₂(SO₄)₃·18H₂O, is obtained by electrolysis of cobaltous sulphate in a platinum dish, which serves as anode, the cathode consisting of a platinum wire immersed in a porous cell containing dilute sulphuric acid. The salt is deposited as blue silky needles round the anode. It is soluble in water, yielding an unstable blue solution which evolves oxygen, the salt being reduced to cobaltous sulphate. Upon exposure to air the crystals gradually decompose. In contact with hydrochloric acid, chlorine is evolved.³

**Cobalt Alums**, M₂SO₄·Co₂(SO₄)₃·24H₂O

Cobaltic sulphate, like the sulphates of rhodium and iridium, unites with the sulphates of the alkali metals to yield a series of well-defined, crystalline salts known as alums. These are isomorphous with those of iron, manganese, chromium, and aluminium, and form an interesting link between these metals and the central vertical column in Group VIII of the Periodic Table, of which column cobalt is the first member.

**Ammonium Cobalt Alum**, (NH₄)₂SO₄·Co₂(SO₄)₃·24H₂O, was first prepared by Marshall,⁴ who, from a peculiar change in colour observed in the electrolysis of a solution of copper-cobalt potassium sulphate, was induced to electrolyse a solution of ammonium and cobalt sulphates, acidified with sulphuric acid in a divided cell.

The solution passes through a series of changes of colour, ultimately becoming greenish blue in consequence of the oxidation of the cobalt to the trivalent state. This suggested the formation of an alum, and by continuing the electrolysis for several days, and then concentrating the solution, blue octahedral crystals were obtained, a few crystals showing faces of dodecahedra and cubes. When thoroughly dry the crystals are not unstable, but their solution is quickly reduced, although the addition of dilute sulphuric acid increases its stability.

**Potassium Cobalt Alum**, K₂SO₄·Co₂(SO₄)₃·24H₂O, was obtained by Marshall mixed with potassium sulphate as blue octahedra in a similar manner to the preceding salt.

**Rubidium Cobalt Alum**, Rb₂SO₄·Co₂(SO₄)₃·24H₂O, and **Cesium Cobalt Alum**, Cs₂SO₄·Co₂(SO₄)₃·24H₂O, have likewise been prepared by electrolysis,⁵ the alums forming at the anode. They crystallise out as minute, deep blue octahedra, stable in dry air, but decomposing in

---

¹ Calcagni and Marrotta, Gazzetta, 1913, 43, [ii], 380.
² Tobler, loc. cit.
moist air to cobaltous and alkali sulphate. In water they rapidly decompose, evolving oxygen, the cobalt being reduced to the divalent cobaltous condition.

COBALT AND SELENIUM

Several selenides of cobalt are known, namely,\textsuperscript{1} Co\textsubscript{2}Se, CoSe, Co\textsubscript{2}Se\textsubscript{4}, Co\textsubscript{2}Se\textsubscript{3}, and CoSe\textsubscript{2}. They are all slowly decomposed by hydrochloric acid and by hydrogen chloride at high temperatures. Hydrogen converts the three last-named selenides into the subselenide at white heat; and if the process is prolonged a mixture of metallic cobalt and selenium ultimately remains. Heated in oxygen, oxides of selenium and cobalt result.

**Cobalt Subselenide,** Co\textsubscript{2}Se.—On reducing either the sesquiselenide or tricobalt tetraseelenide in a current of hydrogen at bright red heat the subselenide is obtained as a brilliant silver-white mass.

**Cobalt Selenide,** CoSe, is yielded in an amorphous condition by heating cobalt in selenium vapour. It also results when hydrogen selenide is passed over cobalt oxide, or preferably the anhydrous chlorate, at bright red heat.

**Tricobalt Tetraseelenide,** Co\textsubscript{2}Se\textsubscript{4}, is obtained in the crystalline form by heating cobalt chloride to dull redness in a mixture of hydrogen selenide or chloride in nitrogen. The resulting crystals are minute regular octahedra, violet-grey in colour and isomorphous with \textit{linneite}, Co\textsubscript{3}S\textsubscript{4}. Density 6.54 at 15° C.

**Cobalt Sesquiselenide,** Co\textsubscript{2}Se\textsubscript{3}, is formed by passing hydrogen selenide over cobalt chloride at dull red heat. It is a grey amorphous mass.

**Cobalt Diselenide,** CoSe\textsubscript{2}, is obtained in a similar manner to the preceding compound as a violet-grey and friable mass which readily loses selenium on heating. Consequently it is necessary to cease heating when the current of hydrogen selenide is stopped, and to cool in an atmosphere of nitrogen.

**Cobalt Selenite,** CoSeO\textsubscript{3}.2H\textsubscript{2}O, obtained by double decomposition of sodium selenite and a soluble cobalt salt, is a beautiful red-violet crystalline powder, insoluble in water.\textsuperscript{2}

**Cobalt Diselenite,** CoSeO\textsubscript{4}.SeO\textsubscript{2}, is prepared by concentration of a solution of the preceding salt in selenious acid at 60° C. It yields microscopic crystals of a deep violet colour, insoluble in cold water, and but sparingly soluble in hot water.\textsuperscript{3}

**Cobalt Triselenite,** CoSeO\textsubscript{3}.2SeO\textsubscript{2}.H\textsubscript{2}O, has been prepared in analogous manner.\textsuperscript{4}

**Cobaltous Selenate,** CoSeO\textsubscript{4}.6H\textsubscript{2}O, is known.\textsuperscript{5} When a neutral solution of this salt is heated in a sealed tube to 250° C., an insoluble basic salt is obtained in the form of small red needles, to which the formula 4CoO.8SeO\textsubscript{3}.H\textsubscript{2}O has been given.\textsuperscript{6}

**Cobaltic Selenate,** Co\textsubscript{2}(SeO\textsubscript{4})\textsubscript{3}.18H\textsubscript{2}O, is an unstable salt obtained by electrolysis of cobaltous selenate at — 10° C.\textsuperscript{7}

\textsuperscript{1} Fonzes-Diacon, \textit{Compt. rend.}, 1900, 131, 704.
\textsuperscript{2} Nilson, \textit{Bull. Soc. chim.}, 1875, 23, 353.
\textsuperscript{4} Nilson, \textit{loc. cit.}
\textsuperscript{5} Topsoe and Christiansen, \textit{Ann. Chim. Phys.}, 1874, 1, 72.
\textsuperscript{6} Bogdan, \textit{Bull. Soc. chim.}, 1893, 9, 586.
\textsuperscript{7} Copaux, \textit{Ann. Chim. Phys.}, 1905, [viii], 6, 508.
COBALT AND TELLURIUM

Cobalt Sesquitelluride is obtained in the hydrated form, Co₅Te₄.4H₂O, as a black precipitate when a solution of sodium telluridé is added to one of cobalt acetate in dilute aqueous acetic acid.¹ Hydrochloric and sulphuric acids are without action upon it, but nitric acid effects its oxidation. At 200° C. it loses water, and at red heat, tellurium; if heated till no further loss in weight occurs, Cobalt Monotelluride, CoTe, is obtained as a grey, crystalline substance of metallic lustre.²

Cobalt Tellurite, CoTeO₄·H₂O, results as a dark purple-blue precipitate when sodium tellurite solution is added to one of cobalt chloride.³ When heated to 300–400° C. it melts without change of colour, and loses water.

COBALT AND CHROMIUM

Neutral solutions of cobalt salts produce with potassium chromate a reddish brown precipitate of hydrated basic cobalt chrome, CoO·CoCrO₄·H₂O. This reaction may be utilised in detecting small quantities of cobalt.⁴

Cobalt Chromate, CoCrO₄, is prepared by heating cobalt carbonate and chromic acid solution for several hours at 185° C. in a sealed tube.⁵ It yields greyish black crystals, readily soluble in hot dilute nitric acid (contrast nickel chromate). The dihydrate, CoCrO₄·2H₂O, is obtained by the interaction of cobaltic acetate and potassium chromate. It yields bronze-coloured prisms or leaflets.⁶

Cobalt Dichromate, CoCr₂O₇·H₂O, is obtained by heating an aqueous solution of cobalt carbonate and chromic acid to a high temperature. It occurs as black deliquescent crystals.⁷

Double Chromates.—Several double chromates containing cobalt have been prepared. Ammonium cobalt chromate, (NH₄)₂CrO₄·CoCrO₄·6H₂O, is obtained by interaction of ammonium chromate and cobalt acetate in aqueous solution at low temperatures,⁸ and the corresponding caesium cobalt chromate is known.⁹ Other complex derivatives have been described.¹⁰

COBALT AND MOLYBDENUM

Numerous complex molybdates of cobalt have been prepared and described.¹¹

Cobalt Molybdate, CoMoO₄, occurs in nature as the mineral pateroïte. It may be prepared artificially by fusing sodium molydate with the chlorides of sodium and cobalt. The product is greyish green in colour. The monohydrate, CoMoO₄·H₂O, has also been prepared.¹²

² Margottet, Thèse de Paris, 1879; Tibbals, loc. cit.
³ Lenher and Wulesensky, see reference and note, p. 124.
⁹ Schulze, Annalen, 1867, 144, 232.
COBALT AND NITROGEN

When cobalt has been maintained at red heat for a considerable time in an atmosphere of pure nitrogen, it becomes less readily attacked by nitric acid, possibly because of the formation of a trace of nitride upon its surface.¹

**Cobalt Nitride**, Co₃N or Co₄N₂, has been prepared by heating cobalt in ammonia vapour to a little below 500° C., the most favourable temperature being 470° C. The metal slowly combines with the nitrogen, some 10-33 per cent. of the gas being absorbed.²

Cobalt nitride is a dull grey powder, readily soluble in hydrochloric and sulphuric acids, yielding cobaltous salts, the nitrogen being liberated as ammonia. At 600° C. it evolves nitrogen, so that the formation of cobalt nitride can only proceed within very narrow limits of temperature. It is completely decomposed when heated in hydrogen or steam; in the latter case the reaction proceeds slowly.

**Cobalt Azoimide**, Co(N₃)₂, and a **Basic Azoimide**, N₃-Co.OH, have been obtained in mixture by Curtius ³ as a violet powder. **Potassium cobalt-azoimide**, KN₃-Co(N₃)₂, is obtained as a bright blue crystalline precipitate when concentrated solutions of the two azoimides are mixed. It explodes at 225° C. The ammonium analogue, NH₄N₃-Co(N₃)₂, has also been prepared.

**Nitro-cobalt**, Co₃(NO₃)₂, is obtained as a black mass when nitrogen peroxide suitably diluted with nitrogen is passed over reduced cobalt.⁴ Water decomposes it vigorously, cobalt nitrate with very little nitrite is produced, together sometimes with a basic salt. When heated in nitrogen it evolves nitrous fumes, then decomposes with almost explosive violence, leaving a mixture of cobalt and its oxide.

**Cobalt Nitrite.**—No nitrites of cobalt have as yet been isolated, although basic salts ⁵ and double nitrites of cobalt and other metals have been prepared.

**Potassium Cobaltous Nitrite**, 2KNO₂·Co(NO₂)₂·xH₂O, is obtained by adding potassium nitrite to a neutral solution of cobalt chloride. It is precipitated as a yellow, hydrated mass, which is soluble in hot water to a red solution.⁶

The Cobalti-nitrites

The cobalti-nitrites have been grouped by Rosenheim and Koppel ⁷ into three classes or types, namely:

1. 3R₂O·Co₂O₃·6N₂O₃ + xH₂O, hexanitrites or yellow cobalti-nitrites.
2. 2R₂O·Co₂O₃·4N₂O₃ + xH₂O, tetranitrites or red cobalti-nitrites.
3. 2R₂O·Co₂O₃·3N₂O₃ + xH₂O, trinitrites.

As the authors point out, it does not appear to be generally possible to determine the constitution of these substances by ordinary physico-

¹ St. Edme, *Compt. rend.*, 1889, 109, 304.
³ Curtius and Bisson, *J. prakt. Chem.*, 1898, [ii], 58, 261.
⁴ Sabatier and Senderens, *Bull. Soc. chim.*, 1893, [iii], 9, 669.
chemical methods, for some of them are insoluble in water, others cannot be redissolved after crystallisation without decomposition, and yet others have not been prepared in a sufficiently pure state. There can be little doubt, however, that they are not simple double salts, but complex bodies, analogous to the cobalti-cyanides, which are discussed in a later section.

**Type 1.** $3R_2O \cdot Co_2O_3 \cdot 6N_2O_3$ or $R_3Co(NO_2)_6$, Cobalti-hexanitrites or Yellow Cobalti-nitrites.

**Potassium Cobalti-nitrite,** $K_3Co(NO_2)_6 \cdot xH_2O$, is the most familiar example of this type. It is also known as cobalt yellow and Fischer's salt in honour of its discoverer.$^1$ It is readily prepared by adding potassium nitrite to an aqueous solution of a soluble cobalt salt acidified with acetic acid. It results in a very pure condition when cobalt carbonate is suspended in an aqueous solution containing an equivalent amount of potassium carbonate or nitrite, and treated with nitrous fumes (resulting from the action of nitric acid upon arsenious oxide) until it has suffered complete decomposition.$^2$ The amount of combined water varies from 0 to 4 molecules according to circumstances.

It is a bright yellow, crystalline powder, insoluble in water, and on account of its stability or "inertness" is used as an artists' pigment. It is a very pure compound when prepared as indicated above, for neither iron nor nickel yields a corresponding derivative; it is therefore valued for painting porcelain, because the blue colour produced on baking is correspondingly pure and beautiful. Furthermore, as has already been mentioned, the salt yields a valuable method of separating nickel from cobalt (see p. 24).

**Sodium Cobalti-nitrite,** $Na_3Co(NO_2)_6$, is best obtained by the action of nitrous acid upon a suspension of cobalt carbonate in the requisite quantity of sodium nitrite solution. The liquor, which at first becomes reddish brown, after several hours assumes a deep brown, almost black colour, is filtered, and the sodium cobaltinitrite in solution is precipitated by the addition of absolute alcohol.$^3$ Cunningham and Perkin$^4$ prepare the salt by dissolving 150 grams of sodium nitrite in hot water and, after cooling to 45–50°C, adding 50 grams of cobalt nitrate until all has dissolved. Glacial acetic acid is now added, and a rapid current of air is aspirated through to remove oxides of nitrogen. On addition of alcohol the sodium cobalti-nitrite separates out.

The salt may also$^6$ be prepared by adding 118 grams of cobalt acetate in dilute acetic acid$^6$ to a solution of 220 grams of sodium nitrite in 400 c.c. of water.

Sodium cobalti-nitrite, as obtained by the foregoing methods, is an orange-yellow powder, readily soluble in water, yielding an intense brownish yellow solution, which decomposes on heating. Dammer

---


$^3$ Cunningham and Koppel, *loc. cit.*


$^6$ 300 c.c. water and 100 c.c. glacial acetic acid.
gives the salt as having \( \frac{22}{3} \) molecules of water. Either the salt to which he refers was not dry, or else the alcohol used in preparing Cunningham's specimens dehydrated them. A characteristic reaction of the solution is the precipitation by it of potassium, ammonium, barium, or lead cobalti-nitrite when added to a solution containing a soluble salt of one of these metals.

**Sodium Potassium Cobalti-nitrite**, \( \text{NaK}_2\text{Co(NO}_3)_6\cdot\text{H}_2\text{O} \), results on adding a solution of sodium cobalti-nitrite to a solution of potassium chloride acidified with acetic acid.\(^1\) The salt is obtained as a yellow precipitate, one part of which requires 20,000 parts of water for its complete solution.\(^1\) The conditions given must be carefully adhered to, otherwise precipitates of varying composition are obtained according to the relative proportions of sodium and potassium.

**Ammonium Cobalti-nitrite**, \( 4\text{NH}_4\text{Co(NO}_3)_6\cdot3\text{H}_2\text{O} \), was first prepared in 1856 by Gibbs and Gent.

Erdmann\(^2\) obtained it by the action of ammonium nitrite upon cobalt chloride solution acidulated with acetic acid. It may also be obtained by adding semicarbazide to a solution of sodium cobalti-nitrite\(^3\) and by double decomposition of solutions of ammonium chloride and sodium cobalti-nitrite; or by addition of nitrous acid to a suspension of cobalt carbonate in the requisite quantity of ammonium nitrite solution.\(^4\) In all three cases the salt is precipitated out.

Ammonium cobalti-nitrite is a yellow powder, almost insoluble in cold water, yielding on warming a yellow solution, which simultaneously decomposes. When dry the salt is quite stable, and may be kept for months without decomposition.

**Barium Cobalti-nitrite**, \( \text{Ba}_2[\text{Co(NO}_3)_6]_2\cdot14\text{H}_2\text{O} \), is most conveniently obtained as a precipitate by addition of sodium cobalticyanide to one of barium chloride. It is yellow in colour, and not quite so stable as the alkali salts.\(^4\)

The corresponding double nitrates of caesium,\(^5\) rubidium,\(^5\) silver,\(^3\) and lead,\(^3\)\(^4\) have also been prepared as insoluble yellow precipitates. Rosenheim and Koppel attribute 12 molecules of water to the last-named, whilst Cunningham and Perkin find 4 molecules of water after the salt has been dried over phosphorus pentoxide.

Type 2. \( 2\text{R}_2\text{O}\cdot\text{Co}_2\text{O}_3\cdot4\text{N}_2\text{O}_5 \) Cobalti-tetra-nitrites or Red Cobalti-nitrates.

**Red Sodium Cobalti-nitrite**, \( 2\text{Na}_2\text{O}\cdot\text{Co}_2\text{O}_3\cdot4\text{N}_2\text{O}_5 \)—To obtain this salt, nitrous acid is added to a suspension of cobalt carbonate in the requisite quantity of sodium nitrite solution until a reddish brown colour is attained. The liquor is evaporated by exposure over sulphuric acid, leaving a reddish brown crystalline powder of the above composition.\(^4\) Alcohol does not precipitate this salt from its aqueous solution, neither is a precipitate obtained with a soluble potassium salt. In both these features, therefore, the red sodium cobalti-nitrite differs from the yellow salt already described. Continued treatment with nitrous oxide converts the red salt into the yellow derivative.

---

\(^1\) T. H. Adie and T. B. Wood, *loc. cit.*
\(^3\) Cunningham and Perkin, *loc. cit.*
\(^4\) Rosenheim and Koppel, *loc. cit.*
\(^5\) Rosenbladt, *Ber.*, 1886, 19, 2531.
Red Barium Cobalti-nitrite, $2\text{BaO} \cdot \text{Co}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$.—On passing nitrous oxide into a suspension of cobalt carbonate in a solution of the requisite quantity of barium nitrite a deep red solution is first formed. This is filtered off before the whole of the cobalt carbonate has dissolved, and evaporated over sulphuric acid at room temperature. At first a little of the yellow barium cobalti-nitrite separates out, but finally deep red crystals are obtained, appearing grey-violet by reflected light under the microscope.\(^1\) The crystals cannot be redissolved in water.

Red Strontium Cobalti-nitrite, $2\text{SrO} \cdot \text{Co}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$, may be prepared in an analogous manner to the barium salt, which it closely resembles.\(^1\)

Potassium and ammonium derivatives of this type have not been isolated. Owing to the insoluble character of their yellow cobalti-nitrites no intermediate red salt seems to be formed during their preparation.\(^1\)

Type 8. $2\text{R}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_3$, Cobalti-tri-nitrites.

Zinc Cobalti-tri-nitrite, $2\text{ZnO} \cdot \text{Co}_2\text{O}_3 \cdot 8\text{N}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$, is obtained by double decomposition of red sodium cobalti-nitrite and zinc chloride solutions. On concentration over sulphuric acid at room temperature small crystals of the zinc salt are formed.\(^1\) These are deep red, almost black in colour, and probably belong to the monoclinic system.

Silver Cobalti-tri-nitrite, $2\text{Ag}_2\text{O} \cdot \text{Co}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, occurs as a brownish grey, microcrystalline precipitate on adding silver nitrate solution to a concentrated solution of zinc cobalti-nitrite.\(^1\)

Cobalto-cobalti-tri-nitrite, $2\text{CoO} \cdot \text{Co}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.—On passing nitrous oxide into a suspension of cobalt carbonate in water a brown solution is obtained from which small, almost black crystals separate on concentration at room temperature. These are usually contaminated with red crystals of cobalt nitrate.\(^1\) Analysis shows the crystals to have the composition

$$2\text{CoO} \cdot \text{Co}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_3 + \text{Co(NO}_3)_2 + 14\text{H}_2\text{O}.$$  

It is uncertain whether the cobalt nitrate is an integral part of the molecule or simply an accidental impurity.

Cobaltous Nitrate, $\text{Co(NO}_3)_2$, may be obtained in the anhydrous condition by the action of nitric anhydride, or a solution of this in nitric acid upon the hydrated salt.\(^2\)

It is a slightly pink powder which decomposes at 100° to 105° C., evolving nitrous fumes.

A solution of cobaltous nitrate in water is readily prepared by dissolving the oxides or carbonate in dilute nitric acid. Slow evaporation yields red, monoclinic prisms of the hexahydrate, $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, of density 1.83.\(^3\) The crystals are very slightly deliquescent in moist air; over concentrated sulphuric acid they effloresce. They melt at 56° C.\(^4\) to a red liquid which, at higher temperatures, thickens, becoming

---

\(^1\) Rosenheim and Koppel, loc. cit.
\(^3\) Marignac, Ann. Mines, 1856, 9, 30.
green, and decomposes evolving brown fumes leaving a residue of oxide. The solubility of the hexahydrate in water is as follows 1:

Temperature °C. . . . . 21 10 4 0 18 41 56
Grams Co(NO₃)₂ per 100 grams solution . . . . 41-55 43-69 44-85 45-66 49-73 55-96 62-88

A solution of cobaltous nitrate saturated at 18° C. has a density of 1.575. Between —21° and 41° C. the composition of the saturated solution at any temperature is given by the expression 1:

\[ \text{Co(NO}_3\text{)}_2 + (12-183 - 0.10177^* \text{H}_2\text{O}. \]

There is no evidence of the existence of a tetrahydrate. When the hexahydrate is kept at 20° to 60° C. in vacuo, or when melted and kept at 70° to 74° C., three molecules of water are lost, and the trihydrate, Co(NO₃)₂.3H₂O, crystallises out in large, rhombic prisms. These melt at 91° C., but do not lose any more water without decomposition.

The solubilities of the trihydrate in water at various temperatures are as follow:

Temperature °C. . 55 62 70 84 91
Grams Co(NO₃)₂ per 100 grams solution 61-74 62-88 64-89 68-84 77-21

There is a break in the solubility curve of the salt at —22° C. which is attributed by Funk to the formation of a nonahydrate at temperatures below this point. This hydrate has not been isolated, although the corresponding nickel salt has been prepared and analysed. Its solubility in water is as follows:

Temperature °C. . . . 26 23-5 20-5
Grams Co(NO₃)₂ per 100 grams solution . 39-45 40-40 42-77

Addition of ammonia in excess to a solution of cobaltous nitrate in the absence of air results in the deposition of rose-coloured crystals of the hexammoniate, \( \text{Co(NO}_3\text{)}_2.6\text{NH}_3.3\text{H}_2\text{O}. \)

A double nitrate of cobalt and bismuth, \( 8\text{Co(NO}_3\text{)}_2.2\text{Bi(NO}_3\text{)}_3.24\text{H}_2\text{O}, \) has been prepared as red crystals, melting at 58° C., and of density 2.48 at 16° C. 4

Basic nitrates have been described. 5

**Cobaltic Nitrate.**—When a concentrated solution of cobaltous nitrate is electrolysed in a divided cell, it assumes a deep indigo-blue colour, but soon returns to its original state when the current is stopped.6 Presumably the colour change is due to the formation in solution of an unstable cobaltic nitrate.

**COBALT AND PHOSPHORUS**

**Cobalt Subphosphide, Co₃P.**—This substance may be obtained by heating finely divided cobalt with copper phosphide in the electric furnace 7; by heating pellets of the metal with red phosphorus in a

---

1 Funk, loc. cit.
4 Urbain and Lacombe, *Compt. rend.*, 1903, 137, 568.
7 Maronneau, *Compt. rend.*, 1900, 130, 658.
COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

crucible, covering with barium chloride, and raising to the melting-point \(^1\); and by exposing reduced cobalt at bright red heat to vapourised phosphorus trichloride, tribromide, or tri-iodide.\(^2\)

Cobalt subphosphide crystallises in grey needles, melting at \(188^\circ\) C., of density 6·3 to 6·6, and of hardness 6. At \(920^\circ\) C. it undergoes polymorphic change. It dissolves in concentrated nitric acid, and is slowly attacked by sulphuric and hydrochloric acids.

**Cobalt Sesquiphosphide**, \(\text{Co}_2\text{P}_3\), is obtained \(^3\) by raising anhydrous cobalt chloride to red heat in phosphorus vapour.

**Tri-cobalt Diphosphide**, \(\text{Co}_3\text{P}_2\), is formed as a black precipitate on reducing cobalt phosphate with a current of hydrogen; and by the action of hydrogen phosphate on cobalt chloride.\(^4\)

**Tetra-cobalt Triphosphide**, \(\text{Co}_4\text{P}_3\), is stated to result as a light grey solid when reduced cobalt is heated to \(500^\circ\) C. in the vapour of phosphorus.\(^5\)

It is doubtful, however, if the last two substances ought to be regarded as separate chemical entities.

**Cobalt Hypophosphite**, \(\text{CoH}_4(\text{PO}_3)_2.6\text{H}_2\text{O}\).—This salt is readily obtained in aqueous solution by double decomposition of solutions of barium hypophosphate and cobalt sulphate; and by dissolving cobalt hydroxide in hypophosphorous acid. On concentration the salt crystallises out with six molecules of water, but becomes anhydrous at \(100^\circ\) C.\(^6\)

**Cobalt Phosphite**, \(\text{CoHPO}_3.2\text{H}_2\text{O}\), is precipitated as a red amorphous compound on addition of ammonium phosphate to an aqueous solution of cobalt chloride.\(^7\) It is also formed on heating freshly precipitated cobalt carbonate with water and phosphorus trichloride,\(^8\) although in this latter case the yield is small. On heating to \(250^\circ\) C. the salt becomes anhydrous and assumes a blue colour. At higher temperatures it becomes incandescent, hydrogen being evolved and a mixture of phosphide and pyrophosphate remaining.

**Cobalt Metaphosphate**, \(\text{Co}_2(\text{PO}_4)_2\), is obtained \(^9\) by evaporating a mixture of cobalt sulphate and phosphoric acid in a platinum dish, and subsequently heating to \(300^\circ\) C. It is deposited as a beautiful, rose-coloured, anhydrous compound, insoluble in water and dilute acids, but soluble in concentrated sulphuric acid.

Several **Orthophosphates** have been described,\(^10\) namely:

\[2\text{CoHPO}_4.5\text{H}_2\text{O}, 2\text{CoHPO}_4.3\text{H}_2\text{O}, \text{and Co}_3(\text{PO}_4)_2.\]

\(^1\) Schenck and Schepel, *Zeitsch. anorg. Chem.*, 1909, 64, 245.

\(^2\) Granger, *Compt. rend.*, 1896, 123, 178.

\(^3\) Granger, *ibid.*, 1896, 122, 1484.


\(^7\) Rose, *ibid.*, 1827, 9, 40.


COBALT AND ARSENIC

Several compounds of cobalt and arsenic have been prepared.

**Tri-cobalt Di-arsenide**, Co$_3$As$_2$, may be prepared by the action of arsenic chloride on metallic cobalt at 800–1400° C.; or by heating mixtures of arsenic and cobalt in hydrogen or carbon monoxide at this temperature. It is also formed when powdered cobalt is heated in hydrogen containing arsenic vapour, and when cobalt arsenate or arsenite is reduced by hydrogen at 900° C. Its density is 7·82, and it loses arsenic when strongly heated.\(^1\)

**Cobalt Arsenite** or **Cobalt Monarsenide**, CoAs, is obtained when the previous compound is heated from 600–800° C., and when cobalt is heated to 275–385° C. in arsenic vapour.\(^2\) It is a grey crystalline powder, of density 7·62, which tarnishes slightly in the air.\(^1\)

A substance having the composition required for a **Cobalt Sesquiar-arsenide**, Co$_2$As$_3$, is formed at 400–600° C., and this, at temperatures below 400° C., is slowly converted into **Cobalt Di-arsenide**, CoAs$_2$. This substance occurs in nature as the minerals *smaltite* and *safflorite*, the former being an important ore of cobalt. It may also be formed by heating cobalt in arsenic vapour from 385–405° C.\(^2\) Its density is 6·97. It is grey in colour, slightly oxidised by air, and decomposes above 400° C.

**Cobalt Tri-arsenide**, Co$_3$As$_2$, is found in nature as the mineral *skutterudite*, and is formed when cobalt is heated in arsenic vapour between 450° and 618° C.\(^2\) **Di-cobalt Pent-arsenide**, Co$_2$As$_5$, has been described.\(^3\)

**Cobalt Arsenites.**—When a dilute solution of cobalt nitrate is precipitated with sodium metarsenite, a violet-blue voluminous deposit of cobalt pyro-arsenite, Co$_2$As$_2$O$_5$ or 2CoO·As$_2$O$_5$, is obtained.\(^3\)

\[2\text{Co(NO}_3\text{)}_2 + \text{Na}_2\text{As}_2\text{O}_4 + \text{H}_2\text{O} = \text{Co}_2\text{As}_2\text{O}_5 + 2\text{NaNO}_3 + 2\text{HNO}_3.\]

At red heat arsenious oxide sublimes, leaving a dark blue residue. An arsenite of composition 3CoO·2As$_2$O$_5$ is obtained as an amethyst-coloured powder by the interaction of solutions of potassium arsenite and cobaltous nitrate.\(^4\) It dissolves in caustic potash to a blue solution; ammonia gives a brown colour, and potassium cyanide a yellow.

**Cobalt Arsenates.**—The *ortho-arsenate*, Co$_3$(AsO$_4$)$_2$.2H$_2$O, occurs in nature as *erythrite* or cobalt bloom in the form of monoclinic crystals isomorphous with vivianite, Fe$_9$(PO$_4$)$_2$.8H$_2$O, and perhaps with nickel ochre, Ni$_3$(AsO$_4$)$_2$.8H$_2$O. Its crystallographic elements are:

\[a:b:c = 0·7987 : 1 : 0·7856. \quad B = 74° 51'.\]

The *pyro-arsenate* Co$_2$As$_2$O$_7$,\(^5\) is known, as also various ammonium arsenates.\(^6\)

An impure basic arsenate is known under the name of *zaffre*, and is used in painting porcelain. It may be obtained by roasting iron-free cobaltite, or by addition of sodium carbonate to a solution of cobaltite in nitric acid, when the zaffre is obtained as a precipitate.

\(^{1}\) Duelliez, *Compt. rend.*, 1908, 147, 424.
\(^{3}\) Reichard, *Ber.*, 1898, 31, 2163.
\(^{4}\) Girard, *Compt. rend.*, 1852, 34, 918; Reichard, *Ber.*, 1894, 27, 1019.
COBALT AND ANTIMONY

Cobalt Antimonide or Cobalt Mono-antimonide, CoSb, may be obtained by direct union of antimony and cobalt, or by heating cobalt in antimony trichloride vapour at 700–1200 °C. It melts at 1191 °C, and has a density of 8.12 at 0 °C. In air it undergoes slight oxidation, burns readily in oxygen, and dissolves in hot, concentrated sulphuric acid.

Cobalt Di-antimonide, CoSb₂, has also been prepared. It melts with decomposition at 879–5 °C; density 7.76 at 0 °C. In its chemical properties it resembles the mono-antimonide.

Cobalt Antimonate, CoSb₂O₅·5H₂O, is obtained by precipitating cobalt acetate with a solution of antimonic acid. The precipitate is rose-coloured, becoming red on drying. When dried over sulphuric acid it loses three molecules of water, yielding the dihydrate, CoSb₂O₅·2H₂O, which at about 300 °C becomes anhydrous.

Cobalt Thio-antimonite, Co₃Sb₂S₆, is obtained by precipitation from a solution of a soluble nickel salt with a dilute solution of potassium thio-antimonite. It is readily oxidised, and always contains potassium if prepared from concentrated solutions.

COBALT AND CARBON

Cobalt Carbide.—Carbon dissolves in molten cobalt, and at very high temperatures the carbide, Co₃C, analogous to cementite, Fe₃C, appears to be formed. It decomposes so rapidly on cooling into cobalt and graphite that the carbide cannot be detected even in quenched specimens.

Cobalt Tetra-carbonyl, Co(CO)₄ or Co₂(CO)₈.—This compound may be prepared by passing carbon monoxide at a pressure of 40 atmospheres over reduced cobalt at 150 °C. The higher the pressure the more rapid is the formation of the carbonyl. It forms as fine, orange-coloured transparent crystals, which are best preserved by hermetically sealing them in a glass tube in an atmosphere of hydrogen or of carbon monoxide. Upon exposure to air decomposition takes place resulting in the formation of a basic cobalt carbonate. With bromine it yields cobalt bromide and carbon monoxide:

$$\text{Co(CO)}_4 + \text{Br}_2 = \text{CoBr}_2 + 4\text{CO},$$

which suggests that the cobalt is divalent, and that the carbonyl is represented by the structural formula:

$$\text{Co}_\text{CO} \overset{\text{CO}}{\text{CO}} \overset{\text{CO}}{\text{CO}}$$

1 Lewkonja, Zeits. anorg. Chem., 1908, 59, 293.
2 Ducelliez, Compt. rend., 1910, 150, 98; 1908, 147, 1048. See also Puschn, J. Russ. Phys. Chem. Soc., 1907, 39, 869.
3 Ducelliez, loc. cit.; Lewkonja, loc. cit.
4 Senderens, Bull. Soc. chim., 1899, 21, 47.
5 Pouget, Compt. rend., 1899, 123, 104.
It is insoluble in water, and but slowly attacked by hydrochloric or sulphuric acid. Owing to its low vapour pressure and ready dissociability cobalt carbonyl is less liable to produce acute poisoning than the corresponding iron and nickel derivatives.\(^1\) The density of the crystals is 1.73, and their melting-point 51°C. The molecular weight determined cryoscopically in benzene solution, indicates that under these conditions the molecule is double, namely, Co\(_2\)(CO)\(_6\). When heated at 60°C, one-quarter of the carbon monoxide is evolved, and jet-black crystals of Cobalt Tri-carbonyl, Co(CO)\(_3\), are obtained. These may be purified by recrystallisation from benzene. Owing to their slight solubility their molecular weight could not be determined. At higher temperatures the tri-carbonyl decomposes to cobalt and carbon monoxide.

Cobaltous Carbonate, CoCO\(_3\).—When cobalt chloride is heated to 140°C with a solution of sodium hydrogen carbonate saturated with carbon dioxide, anhydrous cobalt carbonate is produced as a bright red crystalline powder.\(^2\) By carrying out the reaction at a low temperature the hexahydrate, CoCO\(_3\).6H\(_2\)O, is formed as small crystals.\(^3\) A third hydrate, namely, 3CoCO\(_3\).2H\(_2\)O, is apparently produced when the hexahydrate is maintained at 20-25°C in contact with the saturated solution.\(^4\)

Basic Cobaltous Carbonates.—Several of these have been described, although it may well be that many of them are not really separate chemical entities. The three following substances were described by early workers.\(^5\)

By the action of finely divided aragonite upon concentrated aqueous solutions of cobaltous nitrate, 2CoCO\(_3\).3Co(OH)\(_2\).H\(_2\)O is obtained\(^5\) as a lilac precipitate, which is stable up to 80-85°C, but loses a molecule of water at 95°C. Treatment of more dilute solutions of cobaltous nitrate with aragonite yields CoCO\(_3\).2Co(OH)\(_2\), also a lilac precipitate.\(^5\) CoCO\(_3\).8Co(OH)\(_2\) is obtained as a blue precipitate by the addition of calcite to concentrated cobaltous nitrate.\(^6\) A pink potassium cobalt carbonate, K\(_2\)CoO\(_3\).CoCO\(_3\).4H\(_2\)O, has been prepared. Its solution becomes blue on boiling, returning to its pink colour on cooling. It apparently yields a complex negative ion, Co(CO)\(_3\)\(_{2}\).\(^7\)

Cobaltic Carbonate does not appear to be capable of existing in the solid state. When an oxidising agent, such as hydrogen peroxide or sodium hypochlorite, is added to solutions of cobaltous salts in the presence of excess alkali hydrogen carbonate, a green solution, and in concentrated solution a green precipitate, are obtained.\(^8\) Job\(^9\) has shown that when oxidation is effected with hydrogen peroxide at ordinary temperature the green solution contains trivalent cobalt, and that for each atom of cobalt present, one molecule of carbon dioxide

\(^{1}\) Armit, J. Hygiene, 1909, 9, 249.
\(^{5}\) Beetz, Pogg. Annalen, 1844, 61, 472; Rose, ibid., 1851, 84, 551; Setterberg, ibid., 1830, 19, 55; Winkelblech, Annalen, 1835, 13, 253; Field, J. Chem. Soc., 1861, 14, 48.
is evolved. Durrant concluded that the green precipitate consists essentially of cobaltic carbonate, but Metzl concluded that it is a mixture of cobaltous carbonate and cobalt cobaltite, namely:

$$\text{CoCO}_3 \cdot \text{CoCoO}_3.$$  

**Cobalt and Cyanogen**

**Cobaltous Cyanide**, Co(CN)$_2 \cdot$3H$_2$O, may be precipitated from a solution of the chloride by addition of potassium cyanide. The precipitate, which has a reddish colour, becomes violet at 100° C. It still retains its combined water even at 200° C., but at 250° C. becomes incandescent in air and leaves a black carbonised residue. The original precipitate is soluble in excess of potassium cyanide in consequence of the formation of soluble potassium cobalto-cyanide, K$_2$Co(CN)$_6$. Addition of dilute hydrochloric acid causes the reprecipitation of the cobaltous cyanide unless, in the meantime, the solution has been warmed, thereby oxidising the cobalto-cyanide to cobaltii-cyanide, which is more stable (vide infra).

**Potassium Cobalto-cyanide**, K$_4$Co(CN)$_6$, as mentioned above, is produced when cobaltous cyanide is dissolved in excess of potassium cyanide solution. It may be precipitated from solution by the addition of alcohol. Its aqueous solution contains the ion Co(CN)$_6^{4-}$, so that the formula for the salt is K$_4$Co(CN)$_6$ rather than 4KCN. Co(CN)$_2$. When an air-free aqueous solution of potassium cobalto-cyanide is boiled, hydrogen is evolved, the volume of which equals that of the oxygen absorbed if the solution is rapidly oxidised in air, but to twice that volume during slow oxidation in air. An explanation for this apparent anomaly is given below.

**Nickel Cobalto-cyanide**, Ni$_2$Co(CN)$_6$, is obtained as a golden precipitate on adding nickel sulphate to a solution of potassium cobalto-cyanide. On drying the salt turns green. It dissolves in excess of the potassium salt, yielding **Nickel Potassium Cobalto-cyanide**, K$_2$NiCo(CN)$_6$.

**Cobaltous Cobalto-cyanide**, Co$_2$Co(CN)$_6$, is obtained as a red precipitate on adding cobalt sulphate to a solution of potassium cobalto-cyanide. It dissolves in excess of the potassium salt, yielding **Cobalt Potassium Cobalto-cyanide**, K$_2$CoCo(CN)$_6$.

**Zinc Cobalto-cyanide**, Zn$_2$Co(CN)$_6$, may be prepared as an orange-red precipitate by adding potassium cobalto-cyanide to an excess of zinc sulphate solution acidulated with sulphurous acid. It may be dried without change unless heated to 110–120° C. when it turns violet. It dissolves in excess of the potassium salt, yielding **Zinc Potassium Cobalto-cyanide**, K$_2$ZnCo(CN)$_6$.

**Cobaltii-cyanic Acid, Hydrogen Cobaltii-cyanide**, H$_2$Co(CN)$_6$.H$_2$O.—The free acid may be prepared by decomposing a concentrated aqueous solution of the potassium salt with sulphuric acid, a slight excess of the latter being added. The mixture is warmed, and upon addition of alcohol potassium sulphate separates out, the hydrogen cobaltii-cyanide.

---

remaining in solution. Evaporation and recrystallisation of the resulting product yields the pure acid free from sulphuric acid.\textsuperscript{1} It may also be obtained by decomposing the copper or lead salts in aqueous solution with hydrogen sulphide; and by decomposing the cineol derivative with water.\textsuperscript{2} Hydrogen cobalti-cyanide crystallises from concentrated aqueous solutions in minute, colourless, transparent needles. It has a strongly acid reaction, and readily decomposes carbonates. It dissolves many metals when in a fine state of division, yielding stable salts, hydrogen gas being evolved. It readily absorbs moisture from the air, its crystals deliquesce. It is also soluble in alcohol, but not in ether. At 100° C. its combined water is expelled, and at a somewhat higher temperature hydrogen cyanide is evolved, the acid becoming yellowish in colour. At 190° C. it assumes a green colour, becoming blue at 250° C., and when strongly heated becomes inan- descent, leaving a black, carbonised residue.

**Ammonium Cobalti-cyanide**, (NH\textsubscript{4})\textsubscript{2}Co(CN)\textsubscript{6}.H\textsubscript{2}O, results on neutralising the free acid with ammonia.\textsuperscript{3} A more convenient method consists in decomposing the barium salt with ammonium sulphate solution. On filtering off the insoluble barium sulphate and concentrating the liquor, ammonium cobalti-cyanide crystallises out.\textsuperscript{3} It crystallises in colourless, transparent tablets, which readily dissolve in water, but are less soluble in alcohol. At 225° C. decomposition sets in, ammonium cyanide and carbonate being evolved, leaving a blue residue. The molecule of water cannot be expelled from the salt without simultaneous decomposition.

**Barium Cobalti-cyanide**, Ba\textsubscript{3}[Co(CN)\textsubscript{6}].Aq., is a convenient starting-point for the preparation of other metallic cobalti-cyanides by double decomposition. It may be prepared by adding barium carbonate to a solution of the free acid; but a better method consists in exposing to aerial oxidation a mixture of cobalt sulphate and the cyanides of hydrogen and barium. The salt crystallises out in colourless prisms, which are readily soluble in water, but not in alcohol. They contain some 20 or 22 molecules of water.\textsuperscript{4}

**Potassium Cobalti-cyanide**, K\textsubscript{3}Co(CN)\textsubscript{6}. Gmelin first prepared and described this salt. It is readily produced by the oxidation of the cobalto-cyanide by warming its solution in the presence of air. This reaction is interesting, for when the solution is rapidly oxidised by atmospheric oxygen,\textsuperscript{5} twice as much oxygen is absorbed as corresponds to the equation:

\[ 2K_4\text{Co(CN)}_6 + H_2O + O = 2K_4\text{Co(CN)}_6 + 2\text{KOH}, \]

the excess of oxygen remaining, at the close of the reaction, as hydrogen peroxide.

If, however, the oxidation is allowed to proceed slowly, only a slight excess of oxygen is absorbed, and the amount of hydrogen peroxide resulting is proportionately low.

This is readily explained on the assumption that the reaction proceeds in two stages, in accordance with the theory of Engler,\textsuperscript{6} namely:

\textsuperscript{1} Zwenger. *Annalen*, 1847, 62, 157.
\textsuperscript{2} Baeyer and Villiger, *Ber.*, 1901, 34, 2679.
\textsuperscript{4} Weselsky, loc. cit.; Zwenger, loc. cit.
\textsuperscript{5} Manchot and Herzog, *Ber.*, 1900, 33, 1742.
COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

(i) Direct oxidation of the cobalto-cyanide with a molecule of oxygen according to the scheme:

\[ 2\text{K}_4\text{Co(CN)}_6 + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{K}_3\text{Co(CN)}_6 + 2\text{KOH} + \text{H}_2\text{O}_2. \]

(ii) Indirect oxidation of the cobalto-cyanide with the hydrogen peroxide; thus:

\[ 2\text{K}_4\text{Co(CN)}_6 + \text{H}_2\text{O}_2 = 2\text{K}_3\text{Co(CN)}_6 + 2\text{KOH}. \]

In the first case of rapid oxidation by atmospheric oxygen, the indirect reaction has little time to make itself felt. By slow atmospheric oxidation, however, the indirect reaction has a pronounced effect.

On boiling a solution of potassium cobalto-cyanide, hydrogen is evolved in amount equivalent to the oxygen required for the slow oxidation.

Potassium cobalti-cyanide may also be produced by the addition of dilute acetic acid or hydrogen chloride to a solution of the cobalto-cyanide in excess of potassium cyanide. The acid liberates hydrocyanic acid, which reacts as follows:

\[ 2\text{K}_4\text{Co(CN)}_6 + 2\text{HCN} = 2\text{K}_3\text{Co(CN)}_6 + 2\text{KCN} + \text{H}_2. \]

Upon evaporation the salt may be obtained in yellow, anhydrous crystals isomorphous with potassium ferri cyanide.\(^1\) Density 1-906.

Finally, potassium cobalti-cyanide results when Fischer's salt (potassium cobalti-nitrite) is added in small portions to a warm, concentrated solution of potassium cyanide.\(^2\) Nitrogen or nitrous oxide is evolved and the solution becomes yellow. On cooling, the potassium cobalti-cyanide crystallises out in pale yellow needles.

**Cobalt Cobalti-cyanide**, \(\text{Co}_3[\text{Co(CN)}_6]_2 \cdot 2\text{H}_2\text{O},\) is formed as a rose-coloured, amorphous, and somewhat gelatinous precipitate on adding potassium cobalti-cyanide to cobaltous chloride solution. At 100° C. it loses water, becoming blue \(^3\) in colour; at higher temperatures it becomes anhydrous. On exposure to moist air the blue salt readily absorbs water, becoming pink. Zwenger ascribes 14 molecules of water to the pink salt. It is completely soluble in ammonia. Potassium hydroxide yields blue basic salts which on standing or boiling are converted into rose-coloured cobaltous hydroxide.\(^4\)

**Cupric Cobalti-cyanide**, \(\text{Cu}_3[\text{Co(CN)}_6]_2,\) is obtained as a blue precipitate when potassium cobalti-cyanide is added in sufficient quantity to completely precipitate a copper sulphate solution.\(^5\) It is insoluble in acids, but readily soluble in ammonia. It is decomposed by hydrogen sulphide, copper sulphide being precipitated and hydrogen cobalti-cyanide remaining in solution, from which it can be obtained by concentration. The ammoniacal solution of this salt yields, on evaporation, small blue crystals of a diammoniate, \(\text{Cu}_3[\text{Co(CN)}_6]_2 \cdot 2\text{NH}_3 \cdot 5\text{H}_2\text{O}.\)

**Ferrous Cobalti-cyanide**, \(\text{Fe}_4[\text{Co(CN)}_6]_3,\) is precipitated as a slightly yellow amorphous mass on mixing solutions of ferrous sulphate and potassium cobalti-cyanide.\(^6\) The corresponding ferric salt has also

---

2. Rosenheim and Koppel, *Zeitsch. anorg. Chem.*, 1898, 17, 35; Braun (*Zeitsch. anal. Chem.*, 1868, 7, 313) states that potassium cyanide has no action upon Fischer's salt, but this is incorrect.
5. Zwenger, loc. cit.
been prepared. If precipitated from hot solutions it is yellow in
colour, but in the cold a greenish precipitate is obtained after standing
for a few minutes. This precipitate becomes yellow on boiling.

Nickel Cobalti-cyanide, Ni₅[Co(CN)₆]₂·12H₂O, may be obtained by
precipitating a nickel salt with hydrogen cobalti-cyanide
and or with the
potassium salt. In the latter case the precipitate is not pure, but
contains potassium cobalti-cyanide. The salt is bright blue in colour,
insoluble in water and acids. With ammonia it yields a blue solution
from which crystals of the ammoniate, Ni₅[Co(CN)₆]₂·2NH₃·7H₂O, may
be obtained on concentration.

Silver Cobalti-cyanide, Ag₃Co(CN)₉, is a white curdy precipitate,
insoluble in dilute acids, but readily soluble in ammonia. Potassium
hydroxide converts it mainly into silver oxide. The ammoniacal
solution yields, on concentration, the monammoniate,¹

\[ \text{Ag}_3\text{Co(CN)}_9 \cdot \text{NH}_3 \cdot \text{H}_2\text{O} \]

Lead Cobalti-cyanide, Pb₃[Co(CN)₆]₂·4H₂O, is prepared by the
action of hydrogen cobalti-cyanide upon lead carbonate.¹ It yields
laminated crystals, soluble in about three parts of water. The salt is
not precipitated by adding potassium cobalti-cyanide to a solution of
either lead acetate or nitrate.

Sodium Cobalti-cyanide, Na₃Co(CN)₉·4H₂O, is obtained by
neutralising the free acid with sodium carbonate,² excess of either
reagent being avoided. On concentration the salt crystallises in
transparent, colourless needles which readily dissolve in water, but not
in alcohol. At 100 °C. the salt becomes anhydrous, at higher tempera-
tures it melts and decomposes.

Bismuth, cadmium, cuprous, manganese, mercerious, and zinc
cobalti-cyanides have likewise been isolated.³

The rare earth metals yield heavy, microcrystalline precipitates of
cobalti-cyanides of general formula M₄(CoC₅N₅)₂·9H₂O.

They are but sparingly soluble in water. In dilute hydrochloric acid
their solubilities vary somewhat, the yttrium salt being some three
times as soluble as that of erbium, a fact that enables the two metals
to be separated in this way.³

Cobalt Thiocyanate, Co(CNS)₂·xH₂O, was obtained by Meitzendorff⁴
as a result of dissolving cobalt carbonate in hydrogen thiocyanate, and,
describing it as a yellowish brown crystalline mass, attributed to it the
formula 2Co(CNS)₂·H₂O. Rosenheim and Cohen⁵ prepared the tri-
hydrate, Co(CNS)₂·3H₂O, in an analogous manner as violet crystals,
appearing red by transmitted light, and belonging to the rhombic
system. On solution in water they yield a blue colour which becomes
pink on dilution. In alcohol a deep blue colour is obtained.

Grossmann and Hünseler⁶ prepared the tetrahydrate, Co(CNS)₂·4H₂O,
by double decomposition of solutions of cobalt sulphate and barium
thiocyanate. The solution is at first red, but becomes blue on concen-
tration, and after remaining in vacuo for some time, deposits beautiful

Organic derivatives are described by Wagener and Tollens, Ber., 1906, 39, 410.
⁴ Meitzendorff, Pogg. Annalen. 1842, 56, 63.
wine-red rhombic crystals. These are unstable in air, becoming brown and opaque upon prolonged exposure.\(^1\)

The following double salts have been prepared \(^2\):

- **Potassium cobalto-thiocyanate**, \(K_2\text{Co(CNS)}\_4\cdot4\text{H}_2\text{O}\);
- **Sodium cobalto-thiocyanate**, \(Na_2\text{Co(CNS)}\_4\cdot8\text{H}_2\text{O}\);
- **Ammonium cobalto-thiocyanate**, \((\text{NH}_4)_2\text{Co(CNS)}\_4\cdot4\text{H}_2\text{O}\);
- **Barium cobalto-thiocyanate**, \(\text{BaCo(CNS)}\_4\cdot8\text{H}_2\text{O}\);
- **Silver cobalto-thiocyanate** (dark blue), \(\text{AgCo(CNS)}\_3\cdot2\text{H}_2\text{O}\);
- **Cesium cobalto-thiocyanate** (blue), \(\text{Cs}_2\text{Co(CNS)}\_4\cdot2\text{H}_2\text{O}\);
- **Cesium silver cobalto-thiocyanate**, \(\text{Cs}_2\text{Ag}_2\text{Co(CNS)}\_6\cdot2\text{H}_2\text{O}\) (pink).

**Cobalt Nitro-cyanides**

The close similarity between the constitution of the cobalti-nitrites and cobalti-cyanides naturally leads one to inquire whether or not the radicles \((\text{NO}_3\) and \((\text{CN})\)) are interchangeable. To a certain extent this appears to be the case, for the following salts have been prepared \(^3\):

\[
\text{Na}_6\text{Co}_4(\text{CN})_{10}\text{NO}_2\cdot11\text{H}_2\text{O}, \text{ K}_4\text{Co}_4(\text{CN})_6\text{NO}_2\cdot3\text{H}_2\text{O}, \text{ and Ag}_2\text{Co}_2(\text{CN})_{10}\cdot\text{NO}_2\cdot6\text{H}_2\text{O}.
\]

**COBALT AND SILICON**

**Di-cobalto Silicide** or **Cobalt Subsilicide**, \(\text{Co}_2\text{Si}\), is obtained in grey metallic crystals of density 7.1 at 17° C. and 7.28 at 0° C. by heating cobalt with 10 per cent. of silicon in carbon crucibles in an electric furnace.\(^4\) It may also be prepared by heating cobalt \(^5\) in the vapour of silicon tetrachloride at 1200–1300° C. It is not magnetic, thereby differing from the corresponding iron compound. It dissolves readily in aqueous hydrogen fluoride; less rapidly in hydrogen chloride. It melts at 1827° C.\(^6\)

**Cobalt Monosilicide**, \(\text{CoSi}\), is formed as prismatic needles by heating cobalt and copper silicide in the electric furnace.\(^7\) It melts at 1800° C. in hydrogen, and has a density of 6.90 at 20° C. When heated in fluorine it incandesces, yielding fluorides. Chlorine decomposes it only at a dull red heat, but it dissolves slowly in aqua regia and more rapidly in concentrated hydrogen chloride. It melts at 1393° C.\(^8\)

**Cobalt Disilicide**, \(\text{CoSi}_2\), results when cobalt is heated in the electric furnace with excess of silicon or with a mixture of copper silicide and silicon.\(^9\) It forms dark crystals, probably belonging to the cubic system; density 5.3; hardness 4.5. Sulphur has no action on it, and oxygen at 1200° C. only effects a superficial oxidation. It incandesces in fluorine if gently warmed; chlorine attacks it at 800° C., and bromine and iodine at dull red heat. Concentrated hydrogen

---


\(^4\) Vigouroux, *Compt. rend.*, 1895, 121, 686.

\(^5\) Vigouroux, *ibid.*, 1906, 142, 685.


\(^7\) Lebeau, *Compt. rend.*, 1901, 132, 556.

fluoride readily attacks it, as also do the fused hydroxides of the alkali metals. Hot concentrated solutions of hydrogen chloride or of the alkali hydroxides attack it only slowly. It melts at 1277° C.\(^1\)

Two other silicides have been described,\(^2\) namely, \(\text{CoSi}_2\) (m.pt. 1807° C.) and \(\text{Co}_3\text{Si}_2\) (formed slowly at 1180–1215° C. in the solid state from \(\text{CoSi}\) and \(\text{Co}_2\text{Si}\)).

**Cobalt Orthosilicate**, \(\text{Co}_2\text{SiO}_4\), is obtained by heating to bright redness a mixture of amorphous silica, and the chloride and oxide of cobalt. Excess of silica is removed by treatment with concentrated soda solution, the residue consisting of the orthosilicate in the form of a violet crystalline powder. The crystals are isomorphous with peridote; density 4·83. They are decomposed by hydrochloric acid.\(^3\)

**Cobalt Fluosilicate**, \(\text{CoSiF}_6\cdot6\text{H}_2\text{O}\), results when cobalt carbonate is dissolved in aqueous hydrofluosilicic acid and the solution allowed to evaporate.\(^4\) It crystallises out in red rhombohedra.

**Smalt** has been known for several centuries, having been discovered by Scheurer in 1540, who sold his secret to England. It is prepared by fusing cobalt oxide with silica (powdered quartz) and potassium carbonate, and is thus really a cobalt glass or silicate. The cobalt oxide employed is in the form of *zaffre* or *safflower*; that is, partially roasted sulphide or arsenide ore, the roasting being continued until the cobalt is mostly present as oxide and only sufficient arsenic is left to combine with such impurities as copper and nickel. The quartz is obtained by heating to redness and then disintegrating by plunging into water, after which it is powdered in a mill.

A mixture of *zaffre*, quartz, and potassium carbonate is now introduced into the small furnace, together with a little white arsenic (arsenious oxide), which combines with the iron, copper, and nickel, etc., present as impurities, causing them to separate as a heavy regulus below the liquid mass of glass, at the bottom of the melting-pots. After being kept at a white heat for some time, the glass is ladled out into cold water, which effects its disintegration. The smalt is then ground and levigated.

Smalt is an extremely permanent and inert pigment of a deep blue colour. Its composition varies considerably, but usually within the following limits:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>66-2–72·11</td>
</tr>
<tr>
<td>Cobalt monoxide</td>
<td>6·75–1·95</td>
</tr>
<tr>
<td>Potash</td>
<td>16·31–1·80</td>
</tr>
<tr>
<td>Alumina</td>
<td>8·64–20·04</td>
</tr>
</tbody>
</table>

It is interesting to note that one part of cobaltous oxide will impart a distinctly blue colour to 250 parts of glass.

---


COBALT AND TIN

A few compounds of cobalt and tin have been described. By fusing together at high temperatures an excess of stannic oxide and cobaltous oxide, using potassium chloride as a flux, Basic Cobalt Stannate, CoSnO₃·CoO or Co₂SnO₄, is obtained.¹ The potassium chloride is removed from the cooled mass with water, whilst warm dilute hydrochloric acid effects the solution of the stannate. The pure salt is dark green in colour; density 6.30 at 18⁰C.

Other salts are Cobalt Stannate,² CoSnO₄·6H₂O; Cobalt Fluostannate, CoSnF₆·6H₂O, and Chlorostannate, CoSnCl₆·6H₂O.³

COBALT AND BORON

By heating mixtures of cobalt and boron in a current of hydrogen at 1100–1200⁰C, du Jassonneix ⁴ has prepared two borides of cobalt, namely, the Sub-boride, Co₂B, and the Di-boride, CoB₃. The former occurs as brilliant steel-grey needles of density 7·9 at 20⁰C. These are oxidised by moist air and readily dissolve in nitric acid. The di-boride represents the extreme limit of combination of boron with iron. Evidence of the existence of a Mono-boride, CoB, has also been obtained.⁵

Cobalt Borates.—Several borates of cobalt have been described. The Tetra-borate, CoO·4B₂O₃·12H₂O, is obtained ⁶ by slow evaporation of a solution of cobalt carbonate in boric acid. The precipitate first formed gradually becomes crystalline, rose in colour, but becoming blue on calcination. The dehydrated salt, CoO·4B₂O₃·10H₂O, has also been prepared.⁶

By fusing cobalt chloride with potassium hydrogen fluoride and boric oxide, two borates have been obtained, namely, 2CoO·B₂O₃ and 3CoO·B₂O₃, the latter as rose-coloured rhombic crystals.⁷ Chloro,⁸ bromo,⁹ and iodo ⁹ borates are known.

DETECTION AND ESTIMATION OF COBALT

Detection.—Dry Tests.—Salts of cobalt are usually of a rose-red colour when hydrated, and yield a beautiful blue colour in the borax bead test provided they are not present in excessive amount, otherwise the bead becomes opaque and appears black. When heated on charcoal with reduction mixture in the blowpipe test, metallic cobalt separates out in the form of small magnetic beads. When strongly heated with alumina a blue colour is produced, known as Thenard’s blue.

Wet Tests.—In qualitative analysis by Wet Methods, it is usual to precipitate cobalt, along with any nickel, zinc, and manganese that may be present, by passage of hydrogen sulphide through an ammoniacal

² Ditte, Compt. rend., 1883, 96, 701.
³ Jörgensen, Bull. Acad. Denmark, 1865, 5, 6.
⁷ Ouvrard, Compt. rend., 1900, 130, 335.
⁸ Rousseau and Allaire, ibid., 1894, 118, 1255; 1894, 119, 71.
⁹ Allaire, ibid., 1898, 127, 555.
solution containing these metals in the presence of ammonium chloride. The sulphides are dissolved in aqua regia, and excess of acid boiled off. Sodium hydroxide or peroxide is now added, whereby the hydroxides of cobalt, nickel, and manganese are precipitated, the zinc remaining in solution. The washed precipitates are dissolved in hydrochloric acid, excess of ammonium acetate added, and the sulphides of cobalt and nickel precipitated with hydrogen sulphide, manganese remaining in solution. It now remains to separate the nickel from the cobalt. This may be effected by Liebig’s Cyanide Process, which consists in dissolving the precipitates in aqua regia or hydrochloric acid with a little bromine, boiling off excess of acid or bromine, nearly neutralising with sodium carbonate, and adding potassium cyanide until the precipitated cyanides are just redissolved. After again boiling, which converts the cobalt into potassium cobalti-cyanide, $K_2CoC_6N_8$, sodium hypobromite is added, which precipitates black hydrated nickel oxide, leaving the cobalt in solution.\(^1\) The solution may now be evaporated to dryness with dilute sulphuric acid, and either tested for cobalt by the dry methods mentioned above, or the presence of cobalt confirmed by any of the reactions:

1. \(\alpha\)-nitroso \(\beta\)-naphthol yields a red precipitate of cobalti-nitroso \(\beta\)-naphthol with acetic acid solutions of cobalt salts (see below).
2. Potassium thiocyanate yields a blue colour with solutions of cobalt salts, a blue alcoholic layer being produced on addition of amyl alcohol or of alcohol and ether to the mixture (see p. 71) and shaking.
3. Potassium nitrite yields a yellow precipitate of potassium cobalti-nitrite, $K_2Co(NO_3)_6$, when added to a solution of a cobalt salt containing free acetic acid (see p. 60).
4. Ammonium sulphide yields a black precipitate when added to an ammoniacal solution of a cobalt salt.

**Estimation.**—Cobalt admits of estimation in a variety of ways, the most important of which, however, are:

**Gravimetric Methods.**—The main difficulty is to obtain the cobalt in the form of one of its compounds entirely free from nickel or other metal. This may be accomplished by the cyanide method described under “Wet Tests” above. The solution, after separation of the nickel, is evaporated with dilute sulphuric acid until white fumes are evolved. On addition of water a solution of cobalt sulphate results, and the cobalt may be precipitated in a variety of ways, for example: as oxide with hypobromites or persulphates.\(^2\) as sulphide, as cobalti-nitroso \(\beta\)-naphthol, or as basic carbonate.\(^3\) In each case the precipitate is ignited and reduced to metallic cobalt in a current of pure hydrogen.

The procedure with \(\alpha\)-nitroso \(\beta\)-naphthol is as follows:\(^4\): When it is added to a solution of a cobalt salt acidulated with acetic acid it yields a voluminous precipitate of cobalti-nitroso \(\beta\)-naphthol. Any nickel originally present remains in solution, a very complete separation of the metals being thereby effected. Indeed, the reaction is so sensitive

---

that a distinct turbidity is produced with such traces of cobalt as fail to be precipitated by the nitrite process described above. The naphthol solution is somewhat unstable, and should be made up fresh once a month by dissolving 4 grams of the solid in 150 c.c. of cold glacial acetic acid, and subsequently diluting with an equal quantity of water.

The requisite amount of this solution is added hot to one containing the nickel and cobalt salts acidulated with acetic acid, and the whole allowed to stand overnight. On filtering, the precipitate is washed with 12 per cent. hydrochloric acid to remove any nickel carried down mechanically with the cobalt, and after washing with water and drying, the whole is incinerated with a little pure oxalic acid, and the cobalt reduced to the metallic condition in a current of hydrogen. Copper, chromium, and iron are also precipitated by the naphthol, and should not, therefore, be present in the original solution.

\( \alpha \)-dimethyl glyoxime may be used for separating small quantities of nickel from cobalt. Excess of the glyoxime is added to a boiling ammoniacal solution of the cobalt salt, when the scarlet nickel \( \alpha \)-dimethyl glyoxime is precipitated. \( \alpha \)-diphenyl glyoxime (\( \alpha \)-benzil dioxime) may be used in a similar manner with corresponding results.

A convenient method of estimating cobalt and nickel in an ore consists in decomposing about one gram of the last named with nitric acid and potassium chlorate and removing the insoluble residue by filtration. The solution is acidified with hydrochloric acid, a little bromine water added, and any iron precipitated as ferric hydroxide by excess of ammonia. The solution is again acidified, and any copper, etc., precipitated with hydrogen sulphide. Ammonium chloride is now added and excess of a 1 per cent. alcoholic solution of dimethylgly oxime to the boiling solution. It is now rendered alkaline with ammonia, allowed to stand for thirty minutes, and the nickel dimethyl glyoxime filtered off in a Gooch crucible, dried at 110° C. for one hour, and weighed. The compound has the formula \( \text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4 \), and contains 20.33 per cent. of nickel. The filtrate containing the cobalt in solution is made strongly acid by addition of concentrated sulphuric acid and evaporated till fumes appear. This destroys the organic matter present. On cooling, dilute hydrochloric acid is added and the whole warmed till all solid matter has dissolved. Its temperature is reduced to 50° C., and a warm solution of nitroso \( \beta \)-naphthol in 50 per cent. acetic acid added until precipitation ceases. After standing an hour at 50° C. the precipitate is washed with dilute hydrochloric acid, then with hot water, and finally ignited, being weighed as \( \text{Co}_3\text{O}_4 \).

Volumetric Methods for the estimation of cobalt have been suggested at various times, but owing to the special conditions that have to be observed, their utility is seriously curtailed.

1 This affords a convenient method of quantitatively determining the amount of nickel in a sample of cobalt. See p. 135.

2 The glyoxime solution is prepared by dissolving 10 grams of the solid in a litre of 98 per cent. alcohol.


Colorimetric Methods have frequently been suggested, but of these, that originated by Skey and studied by several others appears to be the most useful. It hinges on the fact that potassium thiocyanate yields a blue colour with solutions of cobalt salts, due to the formation of cobalt thiocyanate. On adding alcohol and ether to the liquid, a blue layer is produced. This is destroyed by mercuric chloride, sodium acetate, or sodium thiosulphate, and is masked by the presence of iron salts in consequence of the intense red colour of ferric thiocyanate; consequently these substances should not be present when the colorimetric test is applied.

In carrying out the test a small quantity of standard cobalt sulphate solution is taken, and acidulated with dilute sulphuric acid. Ammonium thiocyanate is then added and the volume of the liquid made up to 10 c.c. A mixture of alcohol and ether is now added until the total bulk is 20 c.c. and the blue colour of the supernatant ethereal layer is compared with that from a solution of the liquid to be tested, and which has been treated in a precisely similar manner.

Electrolytic Methods have also been employed.  

1 See Lampadius, J. prakt. Chem., 1838, 13, 385; A Muller, ibid., 1853, 60, 474; Skey, Chem. News, 1867, 16, 201.
4 See Mellor, opus cit.
CHAPTER III
NICKEL AND ITS COMPOUNDS

NICKEL
Symbol, Ni. Atomic Weight, 58·68 (O = 16)

Occurrence.—Nickel is a frequent constituent of meteorites (see Part II), in which it usually occurs alloyed with iron in amounts ranging to upwards of 20 per cent. It is also present in the combined state in a considerable number of terrestrial minerals, both as an essential and as a minor ingredient. Thus the *nickeliferous magnetic pyrites* of Pennsylvania contain nickel up to some 5-6 per cent., whilst in Ontario *nickeliferous copper pyrites* are worked with only 2-6 per cent. of nickel. Many igneous rocks contain traces of nickel, Clarke 1 finding 0·0274 per cent. of nickel oxide as the mean of 262 analyses. The sulphide, NiS, occurs as *millerite*, *nickel pyrites*, or *nickel blende*, crystallising according to the hexagonal system; fine acicular structures occur in clay ironstone at Merthyr Tydvil; hardness 3·5; density 4·6–5·6. It is brassy-yellow in colour, easily fusible, and possessed of metallic lustre. The same sulphide associated with iron occurs in the mineral *Pentlandite*, NiS.2FeS, which is cubic; hardness 3·5; density 4·6. Pentlandite was for some years worked at Glen Essochossan, Inveraray, and contained some 14 per cent. of nickel.

Other sulphides are *Folgerite*, NiS·FeS, named after the then Chief of the American Navy Bureau; hardness 3·5; magnetic in mass, but not in small grains. *Blueite*, named after one of the chief Canadian Mining Commissioners, is NiS.2FeS. It is not magnetic; hardness 3–5; density 4·2. *Whartonite*, NiS.7FeS; density 3·73; hardness 4.

Nickel sulphate, NiSO₄.7H₂O, is occasionally found as the orthorhombic mineral *moresonite* or *pyromelane*, and probably results from oxidation of the sulphide. It occurs at Cape Ortegal in Spain, and at Reichelsdorf (Hesse); density 2·0. Nickel telluride, Ni₂Te₂, is found as *melonite* in California, in steely grey hexagonal crystals.

Combined with arsenic, nickel occurs in the mineral *niccolite*, *nickeline*, or *copper nickel*, NiAs. It is rarely crystalline, but when it is the form is hexagonal; hardness 5·5; density 7·5. Its coppery red hue is characteristic, only two other minerals, namely, copper arsenide and *breithauptite* or nickel antimonide, NiSb, bearing any resemblance to it. This latter mineral occurs at Andreasberg, in the Harz, is usually massive, and often associated with a considerable amount of lead sulphide. Crystals are rare; hexagonal.

*Temiskamite*, Ni₄As₄₃, is a silver-white mineral, with a tinge of red, which rapidly tarnishes. Hardness 5·5; density 7·901. It is found in calcite veins in Ontario.² Possibly this mineral is the same as *Maucherite*, a nickel arsenide found in Thuringia.³ The diarsenide *chloanthite* or *white

---

nickel, NiAs₂, occurs at Cobalt, Ontario. It crystallises in imperfect cubes and cubo-octahedra, and is isomorphous with smaltite, CoAs₂, with which it forms numerous intermixtures. It is tin-white in colour; hardness 5-5; density 6-5. An orthorhombic diarsenide of nickel is known as Rammelsbergite, NiAs₂. Gersdorffite comprises massive ores of nickel in the form of sulphide and arsenide in varying proportions, and intermixed with iron and cobalt. Density 5-9. Other minerals are Ullmanite or nickel stibine, NiSbS, found in the Harz; density 6-8; hardness 5. Wolfachite, Ni(SbAs)S, and linnite, (CoNiFe)₃S₄. The oxide NiO has been found in octahedra, known as Bunsenite. It was discovered by Bergmann, in Saxony; hardness 5-5; density 6-4. Nicomelane or black nickel is a rare oxide of composition approximating to Ni₂O₃.

Nickel bloom or nickel ochre, Ni₅(AsO₄)₂.8H₂O, is an apple-green mineral found at Annaberg, Saxony, for which reason it is frequently known as Annabergite. It is most probably isomorphous with erythrite and vivianite. Its colour is characteristic. Rewdanskite is a hydrate silicate of nickel, iron, and magnesium to which the formula (NiFeMg)₂Si₃O₇.2H₂O is assigned. Garnierite¹ or Noumeite² is a hydrated silicate of nickel and magnesium of varying composition approximating to the formula (NiMg)SiO₃.xH₂O. It occurs at Nouméa, in New Caledonia, and, prior to 1905, was the main source of the nickel of commerce. It also occurs at Riddle (Oregon), Webster (N. Carolina), and Revda in the Urals. It is free from arsenic and sulphur, and cannot, therefore, be regarded as a decomposition product of sulphides or arsenosulphides.³ It is really a product from serpentinite in which the magnesium and iron have been more or less completely replaced by nickel. It is brownish yellow in colour, and contains varying amounts up to 27 per cent. of uncombined water. Density 2-5; hardness 2-5. Genthite, a hydrated nickel magnesium silicate, is closely related to Garnierite. Nickel carbonate is found as Texasite or emerald nickel, an amorphous mineral of composition corresponding to the formula 3NiO.CO₂.5H₂O. Hardness 3; density 2-6.

The presence of nickel in the sun’s photosphere has been demonstrated spectroscopically.⁴

For the sake of convenient reference the foregoing minerals are given in the table on page 80, together with their more important physical constants.

History.—Alloys containing nickel and copper have been known and used for several thousand years as witnessed by the existence of ancient currency dating back several centuries before the birth of Christ. Nevertheless, nickel itself was not recognised or isolated as a separate entity until Cronsted, about A.D. 1750, showed that niccolite or kupfernickel, obtained from a cobalt mine in Sweden, contained a new metal. A few years later he succeeded in isolating this metal in an impure form and termed it nickel. The word nickel is equivalent to “goblin” or “devil,” and the term “kupfernickel” was one of

¹ In honour of Garnier, who discovered it in 1865.
² From Nouméa, the capital and chief town, where the first attempt to smelt the ore on the island of New Caledonia was made in 1879. Liversidge distinguishes between Garnierite and Noumeite, reserving the latter name for the dark green, unctuous variety, and the former for the paler and more rare.
³ Garnier, Compt. rend., 1878, 86, 684.
⁴ Löükýer, Compt. rend., 1878, 86, 317.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical composition</th>
<th>Colour</th>
<th>Density (g/cm³)</th>
<th>Hardness (Mohs' scale)</th>
<th>Crystallographic system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annabergite</td>
<td>(See Nickel ochre)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Black nickel</td>
<td>(See Nioccolane)</td>
<td>—</td>
<td>4.2</td>
<td>3-5</td>
<td>—</td>
</tr>
<tr>
<td>Blueite</td>
<td>Ni₅₂₁₂Fe₂₃</td>
<td>Copper-red</td>
<td>7.5</td>
<td>5.5</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Breithauptite</td>
<td>NiSb</td>
<td>Green</td>
<td>6.4</td>
<td>5.5</td>
<td>Cubic</td>
</tr>
<tr>
<td>Busanite</td>
<td>NiO</td>
<td>Tin-white</td>
<td>6.5</td>
<td>5.5</td>
<td>Cubic</td>
</tr>
<tr>
<td>Chloanthite</td>
<td>NiAs₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Copper nickel</td>
<td>(See Niccolite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Emerald nickel</td>
<td>(See Texasite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Folgoreta</td>
<td>Ni₃FeS</td>
<td>Apple-green to almost white</td>
<td>2.5</td>
<td>2.5</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Garnierite</td>
<td>(NiMg)SiO₄.2H₂O</td>
<td>Grey</td>
<td>5.6-6.2</td>
<td>5.5</td>
<td>Cubic</td>
</tr>
<tr>
<td>Gersdorffite</td>
<td>Ni₄As</td>
<td>Grey</td>
<td>4.9</td>
<td>4.5-5</td>
<td>Cubic</td>
</tr>
<tr>
<td>Kupfernickel</td>
<td>(See Niccolite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Linnæite</td>
<td>(CoNiFe)₉S₄</td>
<td>Grey</td>
<td>4.6</td>
<td>3.5</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Melonite</td>
<td>Ni₃Te₂</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Millerite</td>
<td>NiS</td>
<td>Yellow</td>
<td>4.6-5.6</td>
<td>3.5</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Moresonite</td>
<td>NiSO₄·7H₂O</td>
<td>Green</td>
<td>2</td>
<td>2-2.3</td>
<td>Rhomboic</td>
</tr>
<tr>
<td>Niccolite</td>
<td>NiAs</td>
<td>Copper-red</td>
<td>7.5</td>
<td>5.5</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Nickel bloom</td>
<td>(See Nickel ochre)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nickel ochre</td>
<td>Ni₃(AsO₄)₂.8H₂O</td>
<td>Apple-green</td>
<td>—</td>
<td>—</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Nicheline</td>
<td>(See Niccolite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nioccolane</td>
<td>Ni₄O₃</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Noumeite</td>
<td>(See Garnierite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Pentlandite</td>
<td>Ni₃.2FeS</td>
<td>Bronze</td>
<td>4.6</td>
<td>3.5</td>
<td>Cubic</td>
</tr>
<tr>
<td>Pyromelane</td>
<td>(See Moresonite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Rammelsbergite</td>
<td>Ni₃As</td>
<td>Tin-white</td>
<td>6.9</td>
<td>5.5-6</td>
<td>Rhomboic</td>
</tr>
<tr>
<td>Rewdanskite</td>
<td>(NiFe₂)₉SiO₄·2H₂O</td>
<td>—</td>
<td>7.2</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Temiskamite</td>
<td>Ni₃As</td>
<td>Silver-white</td>
<td>7.9</td>
<td>5.5</td>
<td>—</td>
</tr>
<tr>
<td>Texasite</td>
<td>3NiO.CO₃.5H₂O</td>
<td>Emerald-green</td>
<td>2.5-2.6</td>
<td>3-3.25</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Ullmanite</td>
<td>Ni₃S</td>
<td>Steel-grey</td>
<td>6.3</td>
<td>5</td>
<td>Cubic</td>
</tr>
<tr>
<td>Whartonite</td>
<td>Ni₃S₇FeS₃</td>
<td>—</td>
<td>3-73</td>
<td>4</td>
<td>—</td>
</tr>
<tr>
<td>White nickel</td>
<td>(See Chloanthite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Wolfachite</td>
<td>Ni(ShAs)₈S</td>
<td>Silver-white</td>
<td>6.4</td>
<td>4.5-5</td>
<td>Rhomboic</td>
</tr>
<tr>
<td>Zaratite</td>
<td>(See Texasite)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

depreciation applied to the mineral in question because it appeared to contain copper, yet yielded none. Charleton suggests "Old Nick's copper" as an apt translation of kupfernickel.

In 1775 Bergmann ¹ prepared some fairly pure nickel. In 1804 Richter showed that the metal is malleable, ductile, and possessed of high tensile strength.

Nickel was first refined on a commercial scale at Schneeberg, Saxony, and for some years its chief ores were those occurring in the cobalt deposits of Saxony and Bohemia. In 1838 Swedish pyrrhotite ores were found to contain nickel, and a plant was erected for working them. Nickel was also found in certain Norwegian sulphidic ores, and these soon became the main source of the world's nickel supply, to be superseded in 1877 by the New Caledonian ore, Garnierite. In 1886 sulphidic ores from Sudbury, Ontario, made their appearance on the market, and since 1905 have been the main source of commercial nickel.

Previous to 1879 nickel was only used in the manufacture of alloys such as nickel silver, but Fleitmann in that year showed that the brittle-

ness of the then commercial metal could be removed by the addition of small quantities of magnesium. When refined in this way the metal could be welded, and was almost immediately placed on the market in the shape of cooking utensils. From that time to the present the value of nickel for a large variety of purposes has been increasingly recognised. The advent of the Great European War in 1914 still further enhanced its importance inasmuch as it found an enormously extended application in the manufacture of special steels for naval and military purposes.

Preparation.—For laboratory purposes nickel may be prepared in a variety of ways, such as the reduction of its oxides with carbon, carbon monoxide, or hydrogen. By reduction at low temperatures Magnus succeeded in obtaining pyrophoric nickel, and this has been confirmed by Ipatieff for temperatures below 270° C.

Nickel may also be prepared by electrolysis of ammoniacal, acidified, or neutral solutions of its salts, a process that is used commercially for electroplating. It is precipitated by zinc from ammoniacal solutions of its salts, and is left as a residue on igniting either the oxalate or the double nickel ammonium oxalate. Solutions of nickel salts are reduced by hydrogen when heated under pressure, metallic nickel being precipitated out of solution. Thus a N/5 solution of nickel sulphate deposits metallic nickel at 186° C. in the presence of hydrogen at 100 atmospheres pressure, whilst a similar concentration of nickel acetate deposits a pure nickel under like conditions at 168° C.

THE COMMERCIAL PRODUCTION OF NICKEL

Sources of Nickel for Metallurgical Purposes.—Nickel ores occur in Canada, Norway and Sweden, Borneo, New Caledonia, Cuba, France, Germany, Greece, and the Urals. Most of these deposits, however, are small and unimportant. The chief sources of nickel for industrial purposes are Norway, New Caledonia, and Ontario.

Norway was at one time the greatest producer of nickel, but reached her maximum in 1876, when 42,500 tons of ore were mined, containing some 360 tons of nickel. The ore is sulphidic in character, and associated with pyrrhotite and chalcopyrite. It contains as a rule from 1 to 1.7 per cent. of nickel.

New Caledonia, an island situated in the South Pacific discovered by Captain Cook in 1774, was at one time used as a French convict station. In 1865 Garnier discovered nickel there, but its presence in commercial quantities was not proved until 1874. The following year over 300 tons of ore were exported, an amount that increased to 94,154 tons in 1914. The ore known as Garnierite, in honour of its discoverer, is a hydrated silicate of nickel and magnesium. It contains on an average 1 to 8 per cent. of nickel based on the dry weight after

---

1 See Charpy, Compt. rend., 1909, 148, 560.
5 See p. 100, where references are given.
7 Ipatieff, Ber., 1911, 44, 3452.
9 In 1915 the exportation of ore was only 48,578 tons, but owing to war conditions this cannot be regarded as a normal output.
heating to 100° C. to remove the 25 per cent. of water. The following may be taken as a fairly representative analysis of the dried ore 1:

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount (per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>42-00</td>
</tr>
<tr>
<td>Magnesia</td>
<td>22-00</td>
</tr>
<tr>
<td>Lime</td>
<td>0-10</td>
</tr>
<tr>
<td>Alumina</td>
<td>1-00</td>
</tr>
<tr>
<td>Ferric oxide</td>
<td>15-00</td>
</tr>
<tr>
<td>Nickel oxide</td>
<td>9-00</td>
</tr>
<tr>
<td>Cobalt oxide</td>
<td>0-15</td>
</tr>
<tr>
<td>Manganese oxide</td>
<td>0-70</td>
</tr>
<tr>
<td>Chronic oxide</td>
<td>traces</td>
</tr>
<tr>
<td>Combined water</td>
<td>10-00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99-95</strong></td>
</tr>
</tbody>
</table>

For many years this New Caledonian Garnierite was the chief source of the world’s nickel supply, but since 1905 it has been eclipsed by sulphide ores from Ontario. The Commissioners appointed to investigate and report upon the nickel supplies of Ontario published their opinion in 1917 that 2: “The nickel ore deposits of Ontario are much more extensive and offer better facilities for the production of nickel at low cost than do those of any other country. Nickel-bearing ores occur in many parts of the world, but the great extent of the deposits in this province, their richness and uniformity in metal contents, and the success of the industry, point strongly to the conclusion that Ontario nickel has little to fear from competition.”

The reason for the rapid rise to importance of the Ontario deposits is their tremendous extent. Whilst the New Caledonian ore may be estimated in hundreds of thousands of tons, the Ontario ores in the Sudbury area certainly reach seventy million tons, and possibly extend to at least twice that amount. In 1914 slightly more than one million metric tons of nickel ore were mined in Canada. Sudbury ore consists essentially of three minerals, namely, pyrrhotite, chalcopyrite, and pentlandite, accompanied by more or less rocky material of the nature of granite, quartzite, etc. 3

The pyrrhotite or magnetic pyrites is essentially iron sulphide, Fe₃S₈ or 4FeS·FeS₄; chalcopyrite or copper pyrites, Cu₂S·Fe₄S₃, contains some 35 per cent. of copper, whilst the pentlandite contains the nickel as sulphide associated with iron sulphide, thus, NiS·2FeS, and contains approximately 22 per cent. of nickel.

The origin of the Sudbury ores is a matter of dispute. According to the igneous or magmatic theory the three minerals separated in a molten condition from the rock. An alternative theory suggests that the minerals were deposited as the result of cooling or evaporation of heated waters containing them in solution, and emanating from some deep-seated source of igneous material. 4

2 Opus cit., p. xxv.
3 See Coleman, The Nickel Industry, Department of Mines, Canada, 1913; Barlow, Report on the Nickel and Copper Deposits of Sudbury, Geol. Survey, Canada, 1907.
In 1897 nickel was mined in Kirkcudbrightshire to the extent of 300 tons of ore, but no further output has been recorded. Up to 1890 small quantities of asbolan, containing nickel and cobalt, were mined in Flintshire. These have constituted the only sources of nickel in Great Britain.\(^1\)

No ores are mined in the U.S. for their nickel content, although a few hundred tons are obtained each year as by-product from copper ores. The U.S. is the largest producer of nickel, it is true, but obtains its raw material from Canada.

In 1916, owing to the demand for nickel for war purposes, the production of metallic nickel in Canada exceeded by 21.5 per cent. that of the previous year. The figures are:

\[
\begin{array}{ccc}
& 1915 & 1916 \\
\text{lb. of nickel} & 68,808,657 & 82,958,564 \\
\end{array}
\]

An important discovery of nickel ore is reported by Calkins, of the U.S. Geological Survey, as having been made in San Diego County, California. The ore seems to be similar to the Sudbury deposits, and occurs as an irregular mass in a dark gabbro. Assays of more than 4 per cent. of nickel have been obtained.\(^2\)

Nickel-ore discoveries have been reported also in Silesia, Germany, and in the district of Orivio, Bolivia.

THE METALLURGY OF NICKEL\(^3\)

The processes involved in the reduction of nickel ores vary considerably, both with the chemical composition of the ore employed and the nature of the product required. For example, the Sudbury (Ontario) ores consist essentially of sulphides of nickel, copper, and iron. When pure nickel is required it is, of course, essential to remove the copper and the iron. Sometimes, however, an alloy of nickel and copper, known as monel metal, is desired, and it is usual then to remove the iron and subsequently reduce the mixed sulphides of copper and nickel to the alloy direct. Monel metal is thus known as a natural alloy, inasmuch as the constituent elements have not been individually isolated.

Sometimes oxidised ores, such as Garnierite, are reduced for the direct manufacture of ferro-nickel, but the bulk of nickel ore is utilised in the production of commercial nickel. To this end the methods vary somewhat in detail according to the nature of the ore. Most processes, however, may for purposes of description be divided into two sections comprising (I) the production of Bessemerised matte, and (II) the reduction of this matte to metallic nickel, a process usually termed refining.

I. The Production of Bessemerised Matte

(1) Treatment of Sulphide Ores containing Copper.—Owing to the fact that the most important supplies of nickel ores consist of nickelifero\(\text{u}^1\)ous pyrites from Sudbury (Ontario), the method adopted by

---

\(^1\) See *J. Chamber Commerce*, 1916.
\(^3\) For further details the reader is referred to the *Report of the Royal Ontario Nickel Commission*, Toronto, 1917; *The Metallurgy of the Non-Ferrous Metals*, by Gowland (Chas. Griffin and Co., 2nd ed., 1918); *Applied Electro-chemistry*, by Allmand (Arnold, 1912; *The Nickel Industry*, by Coleman (Ottawa, 1913)
the Canadian Copper Company for the preparation of Bessemerised matte may here be advantageously described in considerable detail.

_Epitome of Process._—The ore is first dressed, roasted, and then smelted in blast or reverberatory furnaces to a ferruginous matte consisting essentially of sulphides of copper, nickel, and iron. This is then oxidised in a blast of air in a converter in an analogous manner to the production of steel by the basic Bessemer process. By this means practically all the iron is removed, and as much sulphur as possible without excessive loss of nickel. On an average the product contains approximately:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel and copper</td>
<td>80 per cent.</td>
</tr>
<tr>
<td>Sulphur</td>
<td>20</td>
</tr>
<tr>
<td>Iron</td>
<td>0.5</td>
</tr>
</tbody>
</table>

and such traces of gold, silver, and metals of the platinum group as can be recovered by refining. The matte is then ready to be refined, for, unlike copper, nickel cannot be obtained from its sulphide by mere oxidation since nickel sulphide and oxide do not interact to form metallic nickel.

_Dressing_ the ore consists in hand-picking to remove obvious impurities. This may become an important operation in the future, should it become necessary to utilise less pure ores. Magnetic concentration has been tried, but has not proved successful.

_Roasting._—This is frequently carried out in piles measuring 60 feet by 100 feet in area and 8 feet in height. Such piles contain roughly 2500 tons of ore, and are constructed by first laying a wooden foundation 12 to 18 inches deep, covering with coarse ore, then with medium size, and lastly with "fines" which cover the entire pile and regulate the speed of combustion. The coarse ore amounts to two-thirds of the whole. In order that the fire may penetrate rapidly to the interior and afford a more uniform combustion, flues are let into the wooden foundation and filled with small wood.

The wood burns out in about sixty hours after lighting, but the ore continues to burn for three or four months, its speed of combustion being regulated by control of the draught. The outside portions of ore assume a reddish tint in consequence of the oxidation of iron; frequently the interior of lumps of ore remain unchanged throughout.

On the average, however, the sulphur content is reduced from 23 per cent. in the raw ore to 10 or 12 per cent. in the roasted material.

Roasting in open piles is not very efficient. Exposed to all climatic variations its regulation is complicated. Some of the sulphides are oxidised to soluble sulphites and sulphates which dissolve in rain, etc., and are thus washed away and lost. What the actual loss through this cause may be, is uncertain, but it probably amounts to about 1½ to 2 per cent. of nickel plus copper, the nickel losses being greater than copper, even although the latter element is present in greater abundance. In Norway the open roast-heap practice has been discontinued. As mentioned above, this method of roasting utilises only a relatively small proportion of finely divided ore or fines, the bulk of the pile consisting of rough and medium-sized ore.

Wedge 1 furnaces are employed when fines alone require to be dealt with, and are more efficient than open practice. The ore if over-size

1 See A. W. G. Wilson, _Pyrites in Canada._
is ground in ball mills, transferred to the furnace, and heated first with oil to the desired temperature and maintained at that point with coal fuel. The sulphur content of the ore is reduced to 7 per cent. and less.

Smelting is carried out either in blast or reverberatory furnaces. In the former case the blast-furnaces 1 are rectangular in shape, some 19 feet in height and capable of dealing with 500 tons of charge per day of twenty-four hours. The ores are blended in order to be self-fluxing. If insufficiently roasted during the previous operation further oxidation during smelting is essential, for which purpose quartz is added, the rapidity of smelting being thereby decreased. In this way some 50 per cent. of the iron and sulphur can be oxidised away, a basic ferrous slag being produced.

A typical charge consists of 2:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke</td>
<td>11</td>
</tr>
<tr>
<td>Roasted ore</td>
<td>80.7</td>
</tr>
<tr>
<td>Converter slag</td>
<td>16.7</td>
</tr>
<tr>
<td>Converter scrap, limestone, quartz.</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The ingredients being charged into the furnace in the foregoing order.

The blast, supplied through 32 tuyeres at 22 to 35 oz. pressure, amounts to some 24,000 cubic feet per minute. The molten products flow continuously into oval settlers lined with chrome brick, the matte (density 4.6–4.8) settling to the bottom whilst the slag (density 3.7) overflows continuously into 25-ton pots and is carted away. The matte is tapped at intervals into 7-ton ladles, and averages some 25 per cent. of nickel plus copper, in the proportion of 2.1–2.2 of nickel to 1 of copper.

The average working during 1915–1916 yielded, for every 100 tons of ore, 22.7 tons of matte containing 86 per cent. of the nickel and copper contents of the charge, and 98 tons of slag containing 9 per cent. of the nickel plus copper and which are thus lost.

Reverberatory furnaces 3 are particularly suitable for fines and flue-dust from the blast-furnaces. Their walls and roof are lined with silica bricks, and the hearth with silica sand. A typical charge consists of 2:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wedge calcined ore and Wedge flue-dust</td>
<td>64</td>
</tr>
<tr>
<td>Raw fines</td>
<td>23.7</td>
</tr>
<tr>
<td>Blast-furnace flue-dust</td>
<td>12.8</td>
</tr>
</tbody>
</table>

The coal consumed reaches 22.5 per cent. of the weight of the charge. 2

During 1915–1916 on an average each 100 tons of ore yielded 21.3 tons of matte containing 82.6 per cent. of the nickel plus copper, and 93 per cent. of slag containing 10.5 per cent. of the nickel plus copper of the ore.

Bessemerising.—For this purpose basic converters are used. These are cylindrical in shape, lined with magnesite bricks, and measure 30 feet in length and 10 feet in diameter. A stack rises from the centre to enable the gases to escape, and the necessary air-blast is supplied through 44 tuyeres at the rate of 6500 cubic feet per minute, and under a pressure of 10.5 lb.

In beginning a fresh blow, 70 tons of matte from the blast or reverberatory furnace are poured into the converter in the molten

---

1 Silvester, J. Canadian Min. Inst., 1909, 12, 218.
2 Ontario Report, opus cit.
COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

condition, together with 10 per cent. of siliceous flux. The blast is continued for 30–45 minutes and the slag poured off: 5–6 tons of matte and 3 tons of siliceous flux are added and the whole is again blown. This is repeated until some 400 tons of matte have been treated, and occupies about 52 hours. The resulting Bessemer matte weighs 117 tons. The blast oxidises the iron to ferrous oxide, which combines with the silica to form slag. The magnesite is slowly worn away above the tuyeres, but 6000–7000 tons of matte may be made before repair is necessary.

The Bessemer matte which it is desired to produce should not contain more than 80 per cent. of nickel plus copper, otherwise it is too tough for subsequent handling. The iron is removed as completely as possible, but the sulphur retained in order to yield a brittle product.

Usually the matte thus obtained consists of:

<table>
<thead>
<tr>
<th>Element</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>48–55 per cent.</td>
</tr>
<tr>
<td>Copper</td>
<td>25–30</td>
</tr>
<tr>
<td>Sulphur</td>
<td>20</td>
</tr>
<tr>
<td>Iron</td>
<td>0.5</td>
</tr>
</tbody>
</table>

and is now ready for refining.

(2) Treatment of Sulphide Ores free from Copper.—For this purpose nickeliferous magnetic pyrites are used, containing 2 per cent. and upwards of nickel. These are roasted, whereby the sulphur combined with the iron is expelled, the nickel still remaining as sulphide. The resulting nickel-iron matte is now melted in a reverberatory furnace, and the remaining iron sulphide oxidised by a blast of air, or in a converter similar to that already described. In either case the reactions are much the same, a matte of nickel sulphide being left behind. The ferrous oxide combines with silica of the furnace lining and escapes as slag, together with some nickel which has simultaneously oxidised. The slag is therefore worked again for nickel, and the matte is refined.

(3) Treatment of Silicate Ores.—For this purpose Garnierite, a hydrated silicate of nickel and magnesium, is employed (see p. 79), being exported from New Caledonia to Great Britain and Europe, where it is smelted. The ore contains 6–8 per cent. of nickel, and is first smelted in a small furnace with alkali waste (calcium sulphide), or with gypsum (calcium sulphate) and coke. The nickel and iron (associated with it in the ore) are converted into a nickel-iron matte or sulphide, the magnesium and calcium uniting with the silica to form a fusible slag. The matte is now partially oxidised to remove excess of iron, and the resulting product smelted with coke and sand and nickeliferous slags to effect the removal of still more iron. The concentrated matte is finally Bessemerised to nickel sulphide, and refined.

(4) Treatment of Arsenical Ores.—Nickel is also obtained on a small scale from its arsenical ores. These are roasted to remove part of the arsenic and sulphur, smelted with silica and coke to remove iron in the slag, and the crude nickel arsenide thus obtained roasted in a reverberatory furnace to oxidise more iron and remove more arsenic. The last two operations are repeated until the product is sufficiently

1 The composition of nickel matte has been studied by Bornemann (Metallurgie, 1908, 5, 61), who shows that several double sulphides of iron and nickel are capable of existing under well-defined conditions,
free from iron. The mass, which now consists of fairly pure nickel arsenide, is then converted into nickel oxide, and either reduced with carbon in the usual way, or dissolved in hot hydrochloric acid, and any copper, arsenic, bismuth, or antimony precipitated with hydrogen sulphide. The hydrogen sulphide in excess is removed by boiling, and the iron is oxidised with bleaching powder, and precipitated by cautious addition of milk of lime below 40° C. to prevent the simultaneous precipitation of cobalt. More bleaching powder is added, and the temperature raised, whereby the cobalt which separates out first is precipitated as black hydrated oxide.\(^1\) The nickel solution is drained off, the nickel precipitated with milk of lime, and reduced with charcoal to the metal. The oxide of cobalt is frequently not reduced, but placed after washing and igniting direct on the market as oxide.

II. Refining

As has already been mentioned, nickel cannot, like copper, be obtained from its sulphide by mere oxidation of matte, since nickel sulphide and oxide do not interact to yield the free metal. Several processes have therefore been invented with this object in view, the oldest of which is known as:

(1) The Oxford Process.\(^2\)—This consists in heating Bessemer matte with sodium sulphate and coal in a cupola furnace and tapping the product into pots. The product separates into two layers, the lower and denser consisting mainly of nickel sulphide with smaller quantities of the sulphides of copper (and iron). This layer is known as bottoms. The upper layer or tops is more readily fusible, and is composed of double sulphides of copper and sodium (and of iron and sodium). On cooling, the layers are broken apart. The process is repeated four or five times in order to obtain a pure bottoms, which is then roasted to nickel oxide and reduced to the free metal with charcoal. This is effected by mixing the powdered oxide with flour (or molasses, sugar, etc.) and water to a paste, cutting into small cubes and heating in fireclay tubes, with about 25 per cent. of their weight of charcoal, at about 1260° C.—a temperature that is below the melting-point of nickel. The resulting cubes of metallic nickel are then polished in a drum.

In America a higher temperature is used, and the nickel is produced in the liquid state in crucibles in a muffle-furnace, and cast into small rods. The metal obtained in this way may contain 98 per cent. upwards of nickel, its impurities consisting mainly of oxide, iron, and carbon.

The original Bessemer matte usually contains small quantities of gold, silver, platinum, palladium, iridium, and rhodium. Of these the first two “follow” the copper and are sold in blister copper to refiners. The last four metals, namely, those of the platinum group, follow the nickel and are extracted.

(2) The Mond Process\(^3\) is based upon the fact that nickel readily combines with carbon monoxide at 50–80° C. to form a volatile carbonyl compound of composition Ni(CO)\(_4\), which decomposes at higher tem-

---


COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

88 COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

peratures into metallic nickel and carbon monoxide. Bessemer matte from the Sudbury (Ontario) ores is shipped to Swansea (Wales), and nickel extracted therefrom by the Mond process at the Clydach works. The process is conducted in five stages, which may be conveniently represented by means of a diagram as follows:

The modus operandi is as follows:

(1) The matte is roasted, whereby oxides of nickel and copper are produced, and as much sulphur eliminated as possible.

(2) The mass is now treated with hot dilute (10 per cent.) sulphuric acid in lead-lined extractors whereby some 70 per cent. of the copper is dissolved, but only 1–2 per cent. of the nickel. The solution is concentrated and worked for crystals of copper sulphate, of which some 20,000 tons are annually produced at Clydach.

(3) The insoluble residue containing the nickel oxide is washed, and contains some 50 to 60 per cent. of nickel. It is reduced to the metallic condition by water gas or producer gas rich in hydrogen in vertical towers, 40 feet in height and maintained at 350° C., the powdered residue passing down the tower, meeting the ascending reducing gases.

(4) The reduced product is now transferred to the volatiliser, in which it is subjected to the action of carbon monoxide at 50–80° C., volatile nickel carbonyl being produced. After passing down the volatiliser the residue returns to the reducer and back to the volatiliser. This cycle is repeated for from seven to fifteen days. By this means about 70 per cent. of the nickel is extracted, the residue consisting of:

- Nickel ...... 30 per cent.
- Copper ...... 30 „
- Iron ...... 5 „
- Platinum, etc. .. traces

This residue is smelted with gypsum and reducing agents whereby a matter is produced resembling the original Bessemer matte. This is roasted, reduced, and extracted with carbon monoxide again, and the residues, now much poorer in nickel and copper but richer in the platinum metals, are worked for the last named, the principal being platinum and palladium, although iridium, rhodium, and even gold and silver, are present.

(5) Finally the nickel carbonyl passes to the decomposer, which is filled with nickel shot at 200° C. The carbonyl decomposes, depositing nickel on the shot, which is kept moving to prevent its cohering to
one solid mass. The deposit contains 99.8 per cent. of nickel. The carbon monoxide liberated passes back to the volatiliser.

By this means about 5000 tons of nickel are annually produced at Clydach.

(3) Electrolytic Processes.—From a commercial point of view electrolytic processes have not proved as successful as had been anticipated, although laboratory experiments indicate that they might be employed advantageously both for extracting nickel from concentrated matte, and for refining metallic nickel containing precious metals. Electrolytic refining of nickel is carried out in America, the product being very pure and tough. Plates of it can be punched or hammered without cracking.

Several processes have been tried, and the following rank amongst the most successful of them:

The Hybinette Process 1 consists in roasting copper-nickel matte to convert the metals into oxides, and leaching with 10 per cent. sulphuric acid. The copper is thus mostly dissolved out with but little nickel. A further quantity of copper is removed by heating the residue with sulphuric acid to a temperature at which the sulphates become anhydrous, and again leaching with dilute sulphuric acid. After roasting with hydrochloric acid and again leaching, the residue is smelted to metallic anodes and pure nickel obtained by electrolysing.

The Savelsberg-Wannschafl Process 2 consists in treating with chlorine an intimate mixture of nickel matte and water or calcium chloride solution. The matte employed contains some 65 to 70 per cent. of nickel and some iron, but is, commercially speaking, free from copper. The solution thus obtained contains iron and nickel in the form of their chlorides. Sulphuric acid produced by the oxidation of the sulphur is thrown out as insoluble calcium sulphate. The liquid is filtered free from suspended matters, heated to about 65° C., and fresh powdered ore is added. A blast of air is now blown through, whereby the iron is oxidised and precipitated as insoluble ferric hydroxide. The clear solution containing nickel chloride is separated by filtration and electrolysed between graphite anodes and sheet metal cathodes, at a cathodic current density of 1.0 to 1.2 amperes per sq. dcm., and with a potential difference of from 4.0 to 4.5 volts.

The deposited metal contains some 99.9 per cent. of nickel (and cobalt, if originally present) and only the merest traces of iron, copper, silica, etc. It is compact, though somewhat blistered on account of hydrogen bubbles adhering to the cathode and becoming coated with metal.

Browne’s Process, 3 which is made use of by the Canadian Copper Company, consists in desulphurising copper-nickel-iron matte, whereby a product, containing 54 per cent. of copper and 48 per cent. of nickel, together with small quantities of iron and sulphur, results. Half of this is cast into anodes and the remainder is treated with chlorine in brine, whereby the metals are obtained in solution as chlorides. On electrolysising, copper is deposited on to cathodes of the same metal until the proportion of copper to nickel is reduced to 1 in 80. Addition

2 See Zeitsch. Elektrochem., 1904, 10, 821.
3 See Zeitsch. Elektrochem., 1903, 9, 392.
of sodium sulphide precipitates the remaining copper as sulphide, the iron separates as insoluble ferric hydroxide, and a large proportion of the sodium chloride is crystallised out on concentration of the liquors.

The resulting solution of nickel chloride is electrolysed with graphite anodes and nickel strip cathodes, and yields a very pure metal.

In preparing a specimen of pure nickel for atomic weight purposes Winkler employed the following solution:

- 200 c.c. nickel sulphate solution containing 32.84 grams of nickel per litre.
- 30 grams ammonium sulphate.
- 50 grams ammonium hydroxide of specific gravity 0.905.
- 250 c.c. water.

Best results were obtained with a polished nickel cathode employing a current density of 0.5 amperes. On reaching a certain thickness the deposit of nickel peeled spontaneously from off the cathode, separating as white, shining rolls or leaflets in a high state of purity. Heating in hydrogen effected but a minute loss in weight, indicating the presence of only traces of oxide (compare cobalt).

Properties.—Nickel is a white metal, considerably duller than cobalt. It crystallises according to the regular system. Its density has been variously given as 8.279 at 15.5°C (Bottone), 7.5185 at 20°C (Winkler), and 8.8 at 15°C (Copaux). This variation is due partly to the employment of an impure metal and partly to the fact that the density varies appreciably according to the mechanical treatment to which it has been subjected, the density rising on rolling, hammering, etc. This is well illustrated by the following data, which refer to samples of pure nickel wire. The densities have been calculated for a vacuum at 4°C:

\begin{align*}
(1) \quad \text{Nickel wire, cold drawn} & \quad \ldots \ldots \ldots \ldots \ldots \quad 8.7599 \\
& \quad \text{Same wire annealed} \quad \ldots \ldots \ldots \ldots \ldots \quad 8.8489 \\
(2) \quad \text{Nickel wire, twisted} & \quad \ldots \ldots \ldots \ldots \ldots \quad 8.8273 \\
& \quad \text{Same wire annealed} \quad \ldots \ldots \ldots \ldots \ldots \quad 8.8412
\end{align*}

The figure given by Copaux may be taken as a fair mean for the rolled metal, and 8.3 for the cast. The hardness of nickel is 3.5 on Mohs’ scale (Copaux), equivalent to about 80 on the Brinell scale. The tensile strength is about 42.4 tons per square inch for wrought, annealed nickel. Cast nickel can be rolled into sheets of thickness 0.0008 inch, and drawn into wire of diameter 0.0004 inch. It is thus exceedingly malleable and ductile.
The melting-point of nickel has frequently been determined, the most reliable results being as follow:

<table>
<thead>
<tr>
<th>Authority</th>
<th>Melting-point.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruff, Bormann, and Keilig 1</td>
<td>1452° C.</td>
</tr>
<tr>
<td>Burgess and Waltenberg 2</td>
<td>1452 + 3° C.</td>
</tr>
<tr>
<td>Day and Sosman 3</td>
<td>1452-3° C.</td>
</tr>
<tr>
<td>Holborn and Wien 4</td>
<td>1484° C.</td>
</tr>
<tr>
<td>Copaux 5</td>
<td>1470° C.</td>
</tr>
</tbody>
</table>

The first-named temperature, namely, 1452° C., is adopted by the U.S. Bureau of Standards.

Nickel readily dissolves nickel monoxide, the freezing-point being thereby depressed 6 and the metal becoming brittle. This brittleness is removed on addition of a small quantity of magnesium to the molten nickel. It distils in the electric furnace more readily than cobalt, 7 and boils at 2840° C. under 30 mm. pressure. 8 At white heat nickel can be welded with itself, with iron, or with various alloys.

The coefficient of linear expansion of pure nickel between 0° and 300° C. is given by the expression:

\[ \alpha = (1280 + 0.75t + 0.0035t^2) \times 10^{-6}. \]

Above 300° C. this formula does not agree with experiment, 9 and when the temperature reaches 365° to 370° C. there is a sudden change in the coefficient of expansion. This change is of the same magnitude whether the nickel is heated from a lower temperature or cooled from a higher one to this point. No permanent elongation of the nickel is observed after heating, and successive heatings and coolings fail to modify the effect in the least. It would appear, therefore, that these changes are due to some polymorphic alteration in the metal itself, and the results are interesting in view of the different transition temperatures observed when pure iron is heated or cooled through a considerable range, as detailed in Part II of this volume. Also the cooling curve of nickel indicates the existence of a slight break on the difference curve at 360° C. 10

A further point of interest lies in the fact that nickel is magnetic at ordinary temperatures, but not above 360° C. The transition temperature lies between 340° and 360° C. The heat of transformation from the one polymorph into the other is 0.018 calorie per gram. 11

The coefficient of linear expansion with rise of temperature 12 of the commercial metal is approximately 12.52 \( \times 10^{-6} \).

3 Day and Sosman (Amer. J. Sci., 1910, [iv], 29, 93) using the constant volume nitrogen thermometer scale. This is probably the most accurate result.
5 Copaux, loc. cit.
6 Ruer and Kaneko, Metallurgie, 1912, 9, 419.
7 Moissan, Compt. rend., 1906, 142, 425.
8 Ruff and Bormann, Zeitsch. anorg. Chem., 1914, 88, 386.
9 E. P. Harrison, Phil. Mag., 1904. 7, [vi], 626; Tutton (Chem. News, 1899, 79, 229) gives the formula \( a = 0.00001248 + 0.000000148 t \) between 6° and 121° C.
12 Guillaume, Compt. rend., 1912, 154, 748.
The specific heat of nickel varies with its previous mechanical treatment, and is usually taken as 0.108 for ordinary temperatures, that is, between 20° and 100° C. Schmitz gives the value 0.1094 between the same temperatures.

Its true specific heat between 0° and 300° C. is given by the expression:

\[ \text{Specific heat} = 0.10280 + 0.0000941 t. \]

The most intense lines in the spectrum of nickel are as follow:


Nickel, like iron, readily absorbs hydrogen, the extent of occlusion being independent of the superficial area of the metal. It is thus a true case of solution, and the hydrogen may be regarded as behaving like a metal and yielding an alloy. At constant temperature the solubility of the gas both in solid and in liquid nickel is proportional to the square root of the pressure. The general conditions under which such occlusion takes place closely resemble those already detailed for cobalt. The molten metal "spits" on solidifying in an atmosphere of hydrogen, some twelve times its volume of gas being evolved. Carbon monoxide is also absorbed by the molten metal, and is largely liberated on cooling, yielding castings with blowholes. The disintegration of nickel wire when used as a resistance in electric-furnace work is attributable to absorption of gases. When molten, the metal readily absorbs carbon, its melting-point being thereby lowered, and a carbide, Ni₃C, the analogue of cementite, Fe₃C, being formed.

Like iron and cobalt, nickel exhibits passivity, being rendered passive in a variety of ways, such as by immersion in concentrated nitric acid, or by making it the anode in various solutions.

This suggests that the passivity is due to a layer of oxide forming on the surface of the metal and protecting the underlying portions from attack. Such, very possibly, is one explanation, but apparently it does not account for all cases of nickel passivity. Thus Schmidt and Rathert have passivified nickel by friction in an atmosphere of
hydrogen under conditions in which no oxidation could occur. They suggest, therefore, that the hydrogen-catalysis theory applies to nickel, according to which a metal is normally passive, but becomes active under the influence of a catalyst which is presumed to be hydrogen or hydrogen ions.

Two other theories of passivity have been suggested by Reichenstein.\(^1\) namely, that in some cases the passivity is due to a high concentration of adsorbed molecular oxygen, whilst in others it is due to adsorbed atomic oxygen. As in the case of iron, however, it seems improbable that any one theory will account for all the known cases of passivity. It may well be that in certain cases each of the above-named theories holds, and that under the general term of passivity we are dealing with a variety of different phenomena.\(^2\)

Nickel dissolves readily in dilute nitric acid and in aqua regia. When brought into contact with fuming nitric acid it may be attacked vigorously, it may become passive, or it may yield a grey magnetic powder.\(^3\)

Sea-water, dilute hydrochloric or sulphuric acid has very little action on nickel.\(^4\) At the temperature of the water-bath, dilute sulphuric acid containing 63 per cent. of acid exerts the maximum action on nickel.\(^5\) The resistance of the nickel is greatly enhanced by alloying with tungsten, the optimum percentage being 18 of tungsten.

Dilute sulphuric acid to which hydrogen peroxide has been added attacks nickel, but a mixture of peroxide with glacial acetic acid is without action.\(^6\) Potassium hydroxide, even when fused, has no action on nickel, but when fused with caustic soda the nickel is rapidly oxidised.\(^7\) When heated in the form of wire in oxygen it burns like iron, whilst nickel powder prepared by reduction with hydrogen below 270° C. is pyrophoric.\(^8\) At red heat nickel slowly decomposes steam.

When finely divided nickel, obtained by reduction of the hydroxide with hydrogen, is heated in nitric oxide, nitrogen and nickel oxide are produced.\(^9\)

**Nickel as a Catalyst.**—A mixture of nitric oxide and hydrogen passed over reduced nickel yields ammonia. The reaction, which is nearly quantitative, begins at 300° C., but when once it has set in the temperature may be lowered to 120° C. Nitric oxide alone, however, on being passed over reduced nickel does not yield any nitride, nitrite, or nitrate.\(^10\) When sulphur dioxide and hydrogen are passed over nickel at dull red heat, hydrogen sulphide is formed, and hydrogen phosphide results when hydrogen is passed over a mixture of reduced nickel and

\(^{1}\) Reichenstein, Zeitsch. Elektrochem., 1915, 21, 359.


\(^{5}\) Irmann, Metall und Erz, 1915, 12, 358.

\(^{6}\) Salkowski, Chem. Z., 1916, 40, 448.


\(^{8}\) Ipatieff, J. prak. Chem., 1908, 77, 513.


\(^{10}\) Neogi and Adhicáry, Zeitsch. anorg. Chem., 1910, 69, 209.
phosphorus pentoxide at dull red heat. Nitrogen, entirely free from any oxides, does not combine with hydrogen direct, on passage over reduced nickel.

Reduced nickel decomposes acetylene with incandescence, carbon and volatile hydrocarbons resulting. It also catalytically assists the reduction of ethylene by hydrogen to ethane; of nitrobenzene to aniline; of aliphatic aldehydes and ketones to the corresponding alcohols; of carbon monoxide and dioxide to methane; and many other reactions of a like nature. The method is simple, consisting of the passage of hydrogen and the reducible substance in the form of vapour through a column of reduced nickel maintained at a suitable temperature, that of 180° C. being recommended. The nickel is preferably prepared by reduction with hydrogen in the reaction tube itself, the metal obtained by reduction of the green hydroxide below 300° C. being exceedingly active. The halogens and sulphur poison or destroy the activity of nickel, and for this reason it is better to prepare the hydroxide by precipitation from a solution of nickel nitrate than from the chloride or other halogen salt. Nickel reduced at higher temperatures than 800° C. is less active, whilst if reduced at bright red heat it is practically inert. The hydrogen used in the reduction need not be dried, but must be carefully freed from all traces of hydrogen sulphide, phosphide, arsenide, and chloride. This may be effected by passage over copper turnings at dull red heat, and then over moist potassium hydroxide.

When required for the reduction of many substances it is frequently convenient to prepare the reduced nickel by reduction of the carbonate previously scattered over the surface of a suitable material such as infusorial earth or animal charcoal.

Nickel reduced from the carbonate at 450° C. has no action upon a mixture of hydrogen and oxygen at ordinary temperatures, but if distributed over nine times its weight of inert substance it equals colloidal palladium in activity. It is still more active towards organic compounds if reduced at a lower temperature, such as 310° C.

The oxides of nitrogen, N₂O, NO, and NO₂, are readily reduced by hydrogen in the presence of reduced nickel as catalyst, yielding free nitrogen and ammonia. For example:

\[ 2\text{NO} + 2\text{H}_2 = \text{N}_2 + 2\text{H}_2\text{O} \]
\[ 2\text{NO} + 5\text{H}_2 = 2\text{NH}_3 + 2\text{H}_2\text{O}. \]

Both of these reactions occur simultaneously, but the relative proportions of each vary according to circumstances. For example, the condition of the catalyst plays an important part, and two different preparations will not necessarily yield identical results. Also there is an optimum concentration of hydrogen yielding the highest proportion of ammonia, whilst the temperature of the reaction and the velocity of

1 Neogi and Adhicáry, loc. cit.
5 Kelber, Ber., 1916, 49, 55.
6 Cobalt acts in an analogous manner, but less vigorously.
circulation of the gaseous mixture likewise exert an important influence. The most suitable temperature range appears to be 250° to 300° C. Below this range the reduction takes place slowly, whilst, above it, the nickel loses its activity and the ammonia is appreciably dissociated into its constituent elements.

The best results are obtained with nitric oxide, of which 70 per cent. may, under favourable conditions, be transformed into ammonia; whilst only 25 to 39 per cent. of nitrogen peroxide and 3 to 7 per cent. of nitric oxide yield ammonia.\(^1\)

Finely divided nickel is also used commercially in the catalytic hardening of unsaturated fats and oils such as linseed oil and cottonseed oil. This is accomplished by reducing or hydrogenating them by the simple process of suspending the metal in the oils at about 250° C. and bubbling hydrogen through the mixture. The metal assists the oil to unite with the hydrogen, yielding an oil or fat in which all the carbon atoms are saturated.\(^2\) The catalyst is extremely sensitive to small quantities of air, as well as to traces of chlorine and sulphur compounds, which latter may result from the decomposition of nitrogenous material generally present in oils. Bedford and Erdmann\(^3\) recommend the use of oxides of nickel as catalysts in place of the metal itself on the ground that the oxides are less sensitive to gases containing oxygen and sulphur derivatives, and that they enable hydrogenation to proceed more rapidly. All the oxides of nickel appear capable of acting in this manner. With the dioxide and monoxide a temperature of 250° C. is required, but 180° to 200° C. suffices for the suboxide.

There is a conflict of opinion as to the manner in which the reaction takes place. Many investigators\(^4\) favour the view that the oxides only behave catalytically when they contain a certain amount of free, unoxidised metal, which suggests that it is the element itself and not the oxides which behave catalytically. Bedford and Erdmann,\(^5\) on the other hand, believe that no reduction to metallic nickel takes place during hydrogenation, and that when the higher oxides are used they become partially reduced to the suboxide, which forms a colloidal suspension in the oil.

Organic salts of nickel do not themselves act catalytically, but are reduced by hydrogen when suspended in the heated oils, yielding nickel in various stages of oxidation, and these products effect the hydrogenation. Thus nickel formate is reduced by hydrogen at 210° C. in the presence of the oil to nickel suboxide, whilst at 250° C. complete reduction to the metal is effected.

**Physiological Action of Nickel.**—In minute quantities nickel salts do not appear to be toxic, and there appears to be no danger in the use of nickel utensils for cooking foods.\(^6\)

---

Colloidal Nickel is produced when a solution of the carbonyl in benzene is boiled. Carbon monoxide is evolved, and the resulting colloidal solution of nickel is violet-grey in colour.\(^1\) Kelber\(^2\) has prepared colloidal nickel by submitting a solution of nickel formate and gelatin in glycerol at 200° to 210° C. to the action of a stream of hydrogen. A chestnut-brown colour is produced, the solution remaining unaltered in air. It mixes with alcohol, but addition of water, followed by centrifuging, effects the deposition of the colloidal nickel as a dark brown mass containing 25 to 30 per cent. of metal. This, on treatment with dilute acetic acid, with alcohol or with glycerol yields a colloidal solution again.

The gelatin of the original solution may be replaced by gum acacia, and the hydrogen by such reducing agents as formaldehyde, hydrazine hydrate, hydroxylamine, or hypophosphorous acid. Both nickel acetate and freshly precipitated nickel hydroxide behave in an analogous manner to the formate.

When metallic nickel is heated to incandescence and quickly plunged into distilled water, the presence of colloidal metallic and hydroxide particles can be detected by ultra-microscopic examination.\(^3\)

Colloidal nickelous hydroxide is reduced to colloidal nickel by hydrogen in the presence of colloidal palladium as catalyst. The freshly precipitated hydroxide may also be reduced in a similar manner. It is advantageous to add sodium protalbinate to the mixture before reduction in order to increase the stability of the hydrosols produced.\(^4\)

Pyrophoric Nickel.—Nickel that has been reduced by hydrogen at temperatures below 270° C. is a black powder, pyrophoric upon exposure to ordinary air. It does not, however, burn as brilliantly as iron reduced at 440° C. If reduced at 270° to 280° C. it is oxidised by dry air or oxygen only at 350° C. Moisture facilitates the oxidation of reduced nickel, effecting it at lower temperatures. Nickelous oxide is not oxidised either by dry or by moist air within the temperature interval 220° to 480° C.\(^5\)

Atomic Weight.—Approximate Atomic Weight.—That the atomic weight of nickel is approximately 59, and not a multiple or submultiple of this amount, is evident from various considerations:

1. The specific heat of nickel is 0.109. Assuming a mean atomic heat of 6.4, the atomic weight, according to Dulong and Petit's Law, is approximately 58.7.

2. The most appropriate position for nickel in the Periodic Table is, as explained in Chapter I, the end of the first horizontal series of triads in Group VIII. An atomic weight greater than that of cobalt, namely, 58.97, but less than that of copper, namely, 63.57, is thus to be expected.

3. The double salts of nickel sulphate and the alkali sulphates are isomorphous with the corresponding salts of divalent iron and cobalt. By the application of Mitscherlich's Law, therefore, analogous formulæ

---

\(^1\) W. Ostwald, *Kolloid Zeitsch.*, 1914, 15, 204.

\(^2\) Kelber, *Ber.*, 1917, 80, 1509.


\(^4\) Paal, *Ber.*, 1914, 47, 2202. For further particulars see p. 270.

are to be anticipated, according to which the general formula for the salts is:

\[ \text{M}_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}. \]

Analyses of the compounds indicate that the atomic weight of nickel is 58.68.

**Exact Atomic Weight.**—In 1826 Rothoff, in a single experiment, found that 188 parts of nickel monoxide are equivalent to 718.2 parts of silver chloride;

whence \(2 \cdot \text{Ni} = 59.05\)

In 1832, Erdmann and Marchand, by reducing nickelous oxide in hydrogen, obtained values for the atomic weight of nickel varying from 58.2 to 58.6. In 1856, in a single experiment, Deville arrived at a value 59.3 for the atomic weight.

Most of the remaining determinations of the atomic weight of nickel have been made by chemists who have also studied the atomic weight of cobalt. Thus the experimental methods applied to cobalt by Schneider, Marignac, Dumas, Russell, Winkler, Lee, and Zimmermann, and already described in this volume (see pp. 30–38), were also applied by the same workers to nickel. A few other of the earlier determinations remain to be mentioned, namely, Sommaruga’s analyses of nickel potassium sulphate, Baubigny’s and Schützenberger’s analyses of anhydrous nickel sulphate, and Schützenberger’s, Krüss and Schmidt’s, and Mond, Langer, and Quincke’s analyses of nickelous oxide.

The results of these experimenters are summarised in the table on page 98.

The value at present accepted for the atomic weight of nickel rests upon Richards and Cushman’s analyses of anhydrous nickel bromide. The compound was prepared by the direct union of its elements and sublimed in a porcelain tube in a stream of hydrogen bromide and nitrogen. A trace of sodium bromide thus introduced was duly determined and allowed for in the calculations. Two ratios were established by analysing the compound for bromine according to the usual methods, and a third ratio established by reducing the bromide in hydrogen and weighing the residual metal. The final results were as follow:

- 7 expts. \(2\text{Ag} : \text{NiBr}_2 : : 100\cdot000 : 101.270\) \(\text{Ni} = 58.668\)
- 7 expts. \(2\text{AgBr} : \text{NiBr}_2 : : 100\cdot000 : 58.1740\) \(\text{Ni} = 58.665\)
- 8 expts. \(\text{NiBr}_2 : \text{Ni} : : 100\cdot000 : 26.855\) \(\text{Ni} = 58.682\)

The atomic weights given by the first two ratios should be increased by 0.015, to allow for the presence of the trace of sodium bromide present. The third ratio requires no such correction as the weights of the nickel bromide were corrected before computing the ratio. The corrected atomic weight values are accordingly 58.683, 58.680, and 58.682.

1 See Berzelius, *Pogg. Annalen*, 1826, 8, 184.
2 All the atomic weight values in this section have been recalculated, using the following antecedent data: \(O = 16\cdot000, \text{H} = 1\cdot00762, \text{C} = 12\cdot008, \text{N} = 14\cdot008, \text{Cl} = 35\cdot457, \text{Br} = 79\cdot916, \text{I} = 126\cdot92, \text{Ag} = 107\cdot880, \text{S} = 32\cdot065, \text{Au} = 197\cdot2, \text{K} = 39\cdot100, \text{Ba} = 137\cdot37.
### Table: Atomic Weight of Nickel

<table>
<thead>
<tr>
<th>Date</th>
<th>Experimenter</th>
<th>No. of Expts.</th>
<th>Ratio measured</th>
<th>Atomic weight of nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1857</td>
<td>Schneider</td>
<td>6</td>
<td>Ni : 2CO₃ : 100-000 : 151-606</td>
<td>58-049</td>
</tr>
<tr>
<td>1858</td>
<td>Marignac</td>
<td>2</td>
<td>NiSO₄ : NiO : 100-000 : 48-287</td>
<td>58-761</td>
</tr>
<tr>
<td>1860</td>
<td>Dumas</td>
<td>3</td>
<td>2Ag : NiCl₂ : 100-000 : 60-139</td>
<td>58-842</td>
</tr>
<tr>
<td>1863</td>
<td>Russell</td>
<td>13</td>
<td>NiO : Ni : 100-000 : 78-593</td>
<td>58-871</td>
</tr>
<tr>
<td>1866</td>
<td>Sommaruga</td>
<td>6</td>
<td>2BaSO₄ : K₂Ni(SO₄)₂ : 6H₂O : 100-000 : 93-6505</td>
<td>58-872</td>
</tr>
<tr>
<td>1867</td>
<td>Winkler</td>
<td>4</td>
<td>2Au : 3Ni : 100-000 : 45-209</td>
<td>59-435</td>
</tr>
<tr>
<td>1869</td>
<td>Russell</td>
<td>14</td>
<td>Ni : H₂ : 100-000 : 3-4211</td>
<td>58-906</td>
</tr>
<tr>
<td>1871</td>
<td>Lee</td>
<td>6</td>
<td>(C₃₃H₂₆N₂O₁₁)₂H₂Ni₆(CN)₁₂ : 10H₂O : 3Ni</td>
<td>58-025</td>
</tr>
<tr>
<td>1883</td>
<td>Baubigny</td>
<td>2</td>
<td>NiSO₄ : NiO : 100-000 : 48-280</td>
<td>58-740</td>
</tr>
<tr>
<td>1886</td>
<td>Zimmermann</td>
<td>11</td>
<td>NiO : Ni : 100-000 : 78-582</td>
<td>58-704</td>
</tr>
<tr>
<td>1892</td>
<td>Mond, Langer, and Quincke</td>
<td>3</td>
<td>NiO : Ni : 100-000 : 78-845</td>
<td>58-875</td>
</tr>
<tr>
<td>1892</td>
<td>Schützenberger</td>
<td>2</td>
<td>NiSO₄ : NiO : 100-000 : 48-257</td>
<td>58-671</td>
</tr>
<tr>
<td>1892</td>
<td>Krüss and Schmidt</td>
<td>24</td>
<td>NiO : Ni : 100-000 : 78-534</td>
<td>58-536</td>
</tr>
<tr>
<td>1893</td>
<td>Winkler</td>
<td>6</td>
<td>NiO : Ni : 100-000 : 78-444 (reduction)</td>
<td>58-225</td>
</tr>
<tr>
<td>1894</td>
<td>Winkler</td>
<td>6</td>
<td>NiO : Ni : 100-000 : 78-557 (oxidation)</td>
<td>58-616</td>
</tr>
</tbody>
</table>

Hence, the atomic weight of nickel is \( \text{Ni} = 58.68 \), which value is adopted by the International Committee in their Table of Atomic Weights for 1918.

By accepting this figure for the atomic weight of nickel we are at once confronted with a difficulty in so far as the Periodic Table is concerned.

Cobalt, in its properties, is an excellent intermediary between iron and nickel, and, moreover, it is clearly a suitable element to constitute the first of the central vertical triads of Group VIII, namely, Co, Rh, and Ir. Hence, if the Periodic Law holds absolutely, the atomic weight of cobalt should exceed that of iron, but not that of nickel. Either, therefore, the atomic weight of cobalt is slightly too high or that of nickel is slightly too low.

---

On the other hand, it may be that the Periodic Law as usually expressed is imperfect (see p. 3).

**Uses.**—Nickel is used in a considerable number of industries, not the least important of which is electroplating.

Boetger pointed out in 1842 that dense and lustrous deposits of metallic nickel could be obtained electrolytically, and which were capable of extended industrial application on account of their permanence in air and the readiness with which they acquired and retained their polish. In consequence of these properties the process of plating with nickel has become one of considerable commercial importance (*vide infra*).

Nickel finds extensive application in the manufacture of *alloys* such as German silver, constantan, monel metal, invar, and the like. The outbreak of the Great European War in 1914 led to an enormous increase in the production of nickel steels for military and naval purposes.

Coins of pure nickel are recognised currency in Austria-Hungary, France, Germany, Italy, Mexico, and Switzerland. They are hard, but less easy to mint than an alloy containing 75 per cent. of copper, and which has the advantage of being much cheaper; this latter constitutes the bulk of the so-called "nickel" coinage of the world. Nickel-copper alloys containing 22 to 23 per cent. of nickel were used in making coins in 235 B.C. by Euthydemos, the Bactrian king. Other coins containing nickel have been found, of later date than the foregoing, some struck 2 B.C. containing 20 per cent. of nickel, the remainder being copper with traces of iron and cobalt. The United States of America, however, were the first modern nation to introduce a nickel-bronze coinage, namely, in 1857. The alloy contained 12 per cent. of nickel and 88 per cent. of copper. In 1866 the percentage of nickel was raised to 25, that of the copper falling to 75, thereby coming into line with the Belgian coinage introduced in 1861. Other countries followed suit, and it is estimated that the total weight of metallic nickel used in coinage to date (1917) either as pure nickel or in the 25 per cent. alloy has amounted to between 10,000 and 15,000 tons. It is easy to distinguish between pure nickel coins and the alloy inasmuch as the former are readily attracted by a magnet, whereas the latter are not.

The following table gives the number of nickel and nickel-bronze coins struck since their adoption and down to 1914, in a few of the more important countries of the world:

<table>
<thead>
<tr>
<th>Country</th>
<th>Period.</th>
<th>Value.</th>
<th>Pure nickel.</th>
<th>25 % Ni.</th>
<th>75 % Cu.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austria-Hungary</td>
<td>1892–1914</td>
<td>20 hellers</td>
<td>240,270,049</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 &quot;</td>
<td>320,334,709</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

4 Abridged from the *Ontario Report*, pp. 317–319, in the compilation of which the data were obtained from Rigg's *Annual Reports of the Royal Mint*, London, 1911, 1913, and 1914.
It is estimated that up to the end of 1912 some 909,167,567 coins of pure nickel had been issued, and 4,543,799,571 coins of nickel-bronze.  

Owing to its power of resisting corrosion nickel is used in the manufacture of cooking utensils. There is but little likelihood of danger arising in this manner since nickel salts are not toxic in minute quantities.  

In a finely divided condition nickel is used as a catalyst in the hardening of oils, an industry that is important and rapidly growing. Nickel oxide or hydroxide is used by Edison in making depolarising electrodes for storage batteries. It is also employed in the decoration of porcelain, yielding browns, blues, and greens according to the metal with which it is associated, to the glaze, and the amount of oxide taken. It is used in the production of lustre effects on pottery, yielding a light brown lustre on firing.

**Electro-deposition of Nickel.**—The commercial application of this process only dates back to about 1870, for, prior to that date, the difficulty of obtaining sufficiently pure nickel anodes at reasonable prices was an insuperable handicap to their extended use. When, however, improvements were instituted in the metallurgical methods of extracting nickel from its ores which rendered the production of relatively pure nickel possible at a lower cost, the future of the electroplating industry became assured. Nickel is a particularly useful metal

---

<table>
<thead>
<tr>
<th>Country</th>
<th>Period</th>
<th>Value</th>
<th>Pure Nickel</th>
<th>25% Ni 75% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>1861–1910</td>
<td>25 centimes</td>
<td>—</td>
<td>16,043,690</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>—</td>
<td>1,808,670</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>—</td>
<td>154,628,830</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>—</td>
<td>140,398,488</td>
</tr>
<tr>
<td>France</td>
<td>1908–1914</td>
<td>25</td>
<td>40,941,183</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>3,972</td>
<td>—</td>
</tr>
<tr>
<td>Germany</td>
<td>1878–1914</td>
<td>25 pfennige</td>
<td>30,001,796</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>—</td>
<td>25,029,304</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>—</td>
<td>794,688,261</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>—</td>
<td>768,065,497</td>
</tr>
<tr>
<td>Italy</td>
<td>1902–1914</td>
<td>25 centesimi</td>
<td>13,668,000</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>105,229,666</td>
<td>100,000,000</td>
</tr>
<tr>
<td>Switzerland</td>
<td>1887–1914</td>
<td>5 cents</td>
<td>32,500,000</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2½</td>
<td>—</td>
<td>43,500,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 centimes</td>
<td>—</td>
<td>72,000,000</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>1866–1914</td>
<td>5 paras</td>
<td>—</td>
<td>891,748,975</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 centesimos</td>
<td>—</td>
<td>31,378,316</td>
</tr>
</tbody>
</table>

---

1 Bulletin Imperial Institute, 1916, 14, 228.  
2 Lehmann, Arch. Hygiene, 1909, 68, 421.  
3 See p. 95.  
4 Edison, U.S. Patent 1,036,471, August 20, 1912.  
5 Hainbagh, Pottery Decorating (Scott, Greenwood and Son, 1907).  
6 For further details the reader is referred to A Treatise on Electro-Metallurgy, McMillan and W. R. Cooper (Chas. Griffin and Co., 1910); Applied Electro-Chemistry, Allmand (Arnold, 1912); Electro-plating, Barclay and Hainsworth (Arnold, 1912).
for purposes of electro-deposition. It yields a hard coat susceptible to high polishing and extremely resistant to oxidation or tarnishing under ordinary atmospheric conditions. These properties render it particularly suitable both for protective and ornate purposes. In the former capacity it is used as a covering for more readily oxidisable metals such as iron and steel in exposed portions of machinery, to wit, handle-bars, etc., of bicycles and other domestic commodities. For ornate purposes articles of brass and other metals are frequently plated with nickel as, for example, coffee-urns, cheap spoons, pencil-cases, etc. Some 500 tons of metallic nickel are consumed annually in England for electroplating purposes.

As has already been emphasised in connection with the electro-deposition of cobalt, it is essential that certain well-defined rules be adhered to, otherwise the deposited metal yields disappointing results. Thus the surfaces to be coated must be scrupulously clean, otherwise the nickel will flake off. A similar result accrues if the deposit is too thick, whilst if too feeble a current has been employed in the bath the deposited metal is too brittle, and tends to rub off during subsequent polishing.

Much work has been carried out with the object of determining the best conditions under which the electro-deposition of nickel may be effected, and the following is a summary of the results arrived at:

An aqueous solution of a nickel salt, or of a mixture of salts containing nickel, is made, and a nickel anode inserted. The article to be plated is also introduced into the solution and made to serve as cathode.

The anodes should consist of nickel in as high a state of purity as possible, any cobalt or iron remaining in them being deposited at the cathode during plating. The physical condition of the metal is also important. The cast metal, particularly if its surface has been roughened with acid, is very suitable, as it dissolves most easily. The rolled metal, on the other hand, is inclined from its method of preparation to be more uniform in composition and hence less liable to become spongy during working. It is, however, less readily soluble than the cast metal, although more soluble than electrolytic cobalt unless the last named is fresh and thus charged with hydrogen, which assists its solution. In any case it is advisable for the anodic area to exceed the cathodic on account of the inferior solubility of the metal.

The current density must not be too great, for nickel readily becomes passive. Thus, Schoch found that a nickel anode immersed in a normal solution of nickel sulphate at 26°C. only dissolved when the current density did not exceed 0-086 amperes per square decimetre. When the density rose above this value the anode became passive, gaseous oxygen being evolved from the solution.

This tendency to passivity is reduced by rise of temperature, as also by the introduction of other ions, such as those of chlorine and hydrogen. Hence by raising the temperature and adding sodium chloride to the nickel sulphate solution, the deposition may be effected at a greater current density without passivation of the anode taking place.

Although nickel cannot be deposited quantitatively from a solution containing more than small amounts of free acids owing to the liberation of hydrogen, yet feeble acidity is frequently desirable in order to inhibit

the formation of basic salts which would seriously mar the quality of the plating.

Many different solutions have been suggested to meet the foregoing requirements. The simple sulphate, NiSO$_4$.7H$_2$O, is of little value for electroplating unless used in conjunction with other salts such as ammonium sulphate. Barclay and Hainsworth$^1$ have found the following mixture to give excellent results at about $20^\circ$ C.:

\[
\begin{align*}
\text{Nickel ammonium sulphate}, & \quad \text{NiSO}_4\text{(NH}_4\text{)SO}_4\text{.6H}_2\text{O} \quad 12 \text{ oz. or } 375 \text{ grams} \\
\text{Nickel sulphate}, & \quad \text{NiSO}_4\text{.7H}_2\text{O} \quad 3-4 \text{ oz. or } 94-125 \text{ grams} \\
\text{Water} & \quad \text{1 imperial gallon or } 5 \text{ litres or } 1\frac{1}{2} \text{ U.S. gallon}
\end{align*}
\]

With this solution a current density of 5 amperes per square foot may be employed, equivalent to 0.54 amperes per square decimetre. The initial voltage may be 5, falling to 3 volts or somewhat lower when a thin deposit has formed on the cathode.

A second solution recommended by the same authors is as follows:

\[
\begin{align*}
\text{Nickel ammonium sulphate} & \quad \text{312 grams} \\
\text{Nickel sulphate} & \quad \text{125 oz.} \\
\text{Potassium (or sodium) chloride} & \quad \text{31-47 oz.} \\
\text{Water} & \quad \text{5 litres}
\end{align*}
\]

and may be worked with a current density of 10 amperes per square foot. Watts$^2$ has obtained good results with a solution containing:

\[
\begin{align*}
\text{Nickel sulphate}, & \quad \text{NiSO}_4\text{.7H}_2\text{O} \quad 240 \text{ grams per litre} \\
\text{Nickel chloride}, & \quad \text{NiCl}_2\text{.6H}_2\text{O} \quad 20 \text{ oz.} \\
\text{Boric acid}, & \quad \text{H}_3\text{BO}_3 \quad 20 \text{ oz.}
\end{align*}
\]

When thick deposits of nickel are required it is desirable to work at higher temperatures than that of the room,$^3$ otherwise the deposit tends to peel off in thin layers unless the current is exceedingly feeble. This, according to Engemann,$^4$ is due to traces of iron from the electrolyte being deposited in the first layers and setting up strains in succeeding layers which contain less iron.$^5$ With perfectly iron-free anode and electrolyte peeling does not take place so readily. At temperatures ranging from $50^\circ$ to $90^\circ$ C. thick deposits of nickel may be obtained with a current density of 2.5 amperes per square decimetre.$^6$

Recent work on the rapid electro-deposition of cobalt appears to have stimulated further research into the possibilities of increasing the rapidity of nickel deposition, and it would appear that the subject has not yet been exhausted. Watts recommends hot solutions (c. $70^\circ$ C.) of the composition mentioned above and a current density of 200 to 300 amperes per square foot (22 to 33 per square decimetre). He claims that, under these conditions, "the same amount of metal is deposited in five minutes as requires one and a half hours in the 'rapid solutions' now in use at 10 amperes per square foot."

$^1$ Barclay and Hainsworth, *Electro-plating*, p. 279.  
$^4$ Engemann, ibid., 1911, 17, 910.  
$^5$ Since iron is deposited from solution more easily than nickel.  
$^6$ Foerster, loc. cit.
Nickel-plating may be recognised without damaging the plate by moistening with a drop of acid, and absorbing the drop with filter-paper. Ammonia is added to the latter to neutralise the acid, then acetic acid and a drop of dimethyl glyoxime solution (see p. 76). The characteristic red coloration will immediately betray the presence of nickel.\(^1\)

An ingenious method for determining the thickness of nickel-plating is described by Pontio.\(^2\) The nickel-plated article is immersed in concentrated sulphuric acid to remove grease, etc. It is then rinsed with water and dried with a clean cloth. A few drops of a solution containing:

- Nitric acid . . . . . . . 10 c.c.
- Hydrochloric acid . . . . . . 30 c.c.
- Hydrogen peroxide solution . . . . . . 20 c.c.
- Water . . . . . . . . . . . . . . . 50 c.c.

are now applied to a portion of the cleaned surface, and after two minutes a drop of ammonium hydroxide solution is added. One minute later the liquid is poured on to a white porcelain tile, and its colour noted. A blue tint, in the case of a copper foundation, indicates that the nickel-plating is less than one milligram per square centimetre, whilst a brown colour, in the case of an iron foundation, indicates a plating of fewer than 4 milligrams per square centimetre. With thicker deposits the foundation metal has not been reached by the reagent, and only a pale mauve colour, due to nickel, is observable.

By varying the time of action other thicknesses may of course be determined.

**ALLOYS OF NICKEL**

Nickel yields a considerable number of alloys, some of which are of great technical importance. Chief amongst these are the alloys of nickel and iron, known generally as nickel steels and special ferro-alloys. At least half of the world's nickel production is employed in ordinary peace times in the manufacture of these, whilst during the Great European War of 1914 to 1918 probably three-quarters were consumed for this purpose.

Although the term *nickel steel* is frequently used rather loosely, it is preferable to retain the term for those low carbon steels containing not more than 4 to 5 per cent. of nickel. Most ordinary nickel steels contain from \(2\frac{1}{2}\) to \(3\frac{1}{2}\) per cent. of nickel. Steels containing high percentages of nickel may advantageously be termed *high nickel steels*. As examples of these, *invar* and *platinite* may be mentioned. The former contains some 35 per cent. of nickel, 0·5 of manganese, and 0·5 of carbon, the remainder being iron. This alloy melts at 1425° C., and is remarkable for its low mean coefficient of linear expansion, which between 0° and 40° C. is of the order of one-millionth. It is incorrodible and takes a high polish, and is thus particularly valuable for the manufacture of chronometers, etc. The second of the above alloys, namely, platinite, contains about 46 per cent. of nickel, but only 0·15 of carbon. It has approximately the same coefficient of expansion as platinum and glass, and is thus suitable for sealing into glass apparatus. Nickel

1 Bianchi and di Nola, *Boll. chim. farm.*, 1910, 49, 517.
2 Pontio, *Compt. rend.*, 1915, 161, 175.
resistance wire used in electric cookers, flat-irons, etc., contains approximately 25 to 30 per cent of nickel. For further details of nickel steels and ferro-nickels the reader is referred to Part II of this volume.

Various alloys of nickel and copper are of great industrial importance. The two metals mix in all proportions, the nickel reducing the conductivity and increasing the hardness of the copper. The alloys are variously known as cupro-nickel, nickel bronze, and nickel brass, whilst certain of them have special names such as monel metal, Benedict metal, nickel or German silver, etc.

On adding copper to nickel the melting-point falls continuously from that of pure nickel to that of pure copper. All the alloys, therefore, consist of a uniform solid solution throughout.

An alloy containing 20 per cent. of nickel and 80 per cent. of copper, and known as cupro-nickel, is employed in munition work such as the manufacture of bullet jackets. It melts at 1190° C., and has good working properties. It is made by fusing nickel and copper together in the requisite proportions in graphite crucibles, and is teemed at about 1800° C. It is essential to pour at this high temperature, as otherwise the resulting ingots are unsound. As a further precaution a small quantity of deoxidiser is usually added to the molten alloy before pouring, namely, 0·1 per cent. of manganese or small amounts of cupro-manganese.

Benedict metal is manufactured in the U.S.A., their Government specification for the alloy being:

| Nickel | . . . . | 14 to 16 per cent. |
| Copper | . . . . | 84 to 86 |

A very important alloy containing 25 per cent. of nickel and 75 per cent. of copper finds extensive application in the manufacture of currency both in Europe and in the New World. Reference has already been made to this in previous pages. Monel metal is an alloy of nickel and copper made by the Orford Copper Company by direct reduction of the nickel-copper matte obtained from the Sudbury ores (see p. 82). It is therefore termed a "natural alloy." It contains from 60–72 per cent. of nickel, the remainder consisting mainly of copper with iron ranging from 0·5 to 6·5 per cent. The United States Government specification, issued in July 1910, for monel metal requires

<table>
<thead>
<tr>
<th>Ni (minimum)</th>
<th>Cu</th>
<th>Fe</th>
<th>Al</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castings</td>
<td>60</td>
<td>33</td>
<td>6·5</td>
<td>0·5</td>
</tr>
<tr>
<td>Rolled</td>
<td>60</td>
<td>36</td>
<td>3·5</td>
<td>0·5</td>
</tr>
</tbody>
</table>

In appearance the alloy resembles nickel and takes a brilliant polish. It is sometimes difficult to obtain in sound ingots owing to the presence of dissolved gases, although addition of 2 oz. of magnesium to each 100 lb. of molten alloy before pouring tends to reduce the danger.

The chief physical properties of monel metal are:

| Melting-point | . . . . | 1360° C. |
| Density of cast alloy | . . . . | 8·87 |
| Coefficient of expansion per degree Centigrade (20°C.–100°C.) | . . . . | 0·00001375 |
| Tensile strength | . . . . | approx. 35 tons per sq. inch |

1 See p. 99.
Monel metal is used in the manufacture of propellers for United States battleships, etc. Owing to its power of resisting heat Germany employs the alloy for locomotive fire-boxes.

Alloys of nickel, copper, and zinc are known as nickel-silver, and have a large industrial application. One such was known to the Chinese in early times under the name of Packfong, being used for gongs and other musical instruments. Individual specimens exhibit considerable variation in composition, ranging from 8-75 to 31-9 per cent. of nickel.

The manufacture of nickel-silver in Europe was begun in Berlin in 1824, and the fancy names given to the alloy are legion. It is customary in England to prepare the alloy in three stages, and not by melting together the three ingredients in the correct proportions. Thus, copper and nickel are alloyed to form cupro-nickel, and zinc and copper to form brass. The last named is cast into plates, broken up whilst hot, and added to the molten cupro-nickel. This procedure serves not only to yield a more homogeneous alloy, but also reduces the oxidation of the zinc. In Germany, on the other hand, copper and one-third of the requisite quantities of nickel and zinc are melted together under charcoal in a crucible, the remaining two-thirds of zinc and nickel being added after the whole has fused. Owing to the volatilisation of the zinc it is difficult to prepare two samples having the same composition.

The alloy is annealed in a reverberatory furnace in a reducing atmosphere at a temperature ranging from 700° to 900° C. according to the nature of the alloy. In ordinary practice exposure for 20 to 60 minutes to a temperature of 750° C. suffices. Deoxidation with 0-25 per cent. of manganese improves the rolling properties of the finished alloy, and its tensile strength rises distinctly with the nickel content.

Different grades of nickel-silver are recognised in the trade, those manufactured at Birmingham and Sheffield having approximately the following compositions:

<table>
<thead>
<tr>
<th>Extra white metal</th>
<th>Copper per cent.</th>
<th>Nickel per cent.</th>
<th>Zinc per cent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>White metal</td>
<td>50</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Arguzoid</td>
<td>54</td>
<td>24</td>
<td>22</td>
</tr>
<tr>
<td>Best best</td>
<td>48·5</td>
<td>20·5</td>
<td>31</td>
</tr>
<tr>
<td>Firsts or best</td>
<td>50</td>
<td>21</td>
<td>29</td>
</tr>
<tr>
<td>Special firsts</td>
<td>56</td>
<td>16</td>
<td>28</td>
</tr>
<tr>
<td>Seconds</td>
<td>56</td>
<td>17</td>
<td>27</td>
</tr>
<tr>
<td>Thirds</td>
<td>62</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>Special thirds</td>
<td>56</td>
<td>12</td>
<td>32</td>
</tr>
<tr>
<td>Fourths</td>
<td>56·5</td>
<td>11</td>
<td>32·5</td>
</tr>
<tr>
<td>Fifths, for plated goods</td>
<td>57</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>Electrum</td>
<td>51·5</td>
<td>26</td>
<td>22·5</td>
</tr>
</tbody>
</table>

3 The first eleven are given by Hiorns (quoted by Law, Alloys, Chas. Griffin and Co., 2nd ed., 1914). The last alloy is taken from J. Inst. Metals, 1912, 7, 193.
Of the foregoing, the alloy termed "Seconds" is used as the basis in best silver-plate ware, namely, A1 quality. It is also the constituent of nickel-silver table goods such as spoons and forks.

Nickel-silver possesses considerable malleability, ductility, and tensile strength. No compounds of the three constituent metals are formed, and the alloy is a simple, homogeneous, solid solution.

Nickel-silver to which 1 or 2 per cent. of tungsten has been added is known as platinoid. It has a low electrical conductivity, and is therefore used in the manufacture of resistances. In composition it approximates to:

- Copper: 60 per cent.
- Nickel: 14 per cent.
- Zinc: 24 per cent.
- Tungsten: 1–2 per cent.

Argozoil is nickel-silver containing a little lead and tin—about 2 per cent. of each. Other alloys of interest are constantan, manganin, nickelin, and nichrome, approximate analyses of which are given in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Argozoil</th>
<th>Constantan</th>
<th>Manganin</th>
<th>Nickelin</th>
<th>Nichrome</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>14</td>
<td>40</td>
<td>4–40</td>
<td>32</td>
<td>60</td>
</tr>
<tr>
<td>Copper</td>
<td>54</td>
<td>60</td>
<td>60–80</td>
<td>55–70</td>
<td>—</td>
</tr>
<tr>
<td>Zinc</td>
<td>28</td>
<td>—</td>
<td>—</td>
<td>0–13</td>
<td>—</td>
</tr>
<tr>
<td>Lead</td>
<td>2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tin</td>
<td>2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Manganese</td>
<td>—</td>
<td>—</td>
<td>1–12</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Chromium</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>14</td>
</tr>
<tr>
<td>Iron</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>15</td>
</tr>
</tbody>
</table>

Of the foregoing alloys nichrome possesses many interesting features. It is now well known for its electrical resistance, and is useful in the construction of electric heating appliances, such as air ovens, muffle and tube furnaces, for use in the chemical laboratory.

It is easily cast, and as it neither oxidises nor scales it is particularly serviceable for fire-boxes, proving far longer-lived than cast steel ones; they do not warp or bulge, and retain their strength and shape at high temperatures. They may be quenched in water whilst red hot, and, owing to the greater durability of the alloy, they may be made considerably thinner than is usual with other metals. Nichrome loses but little of its strength at 950° to 980° C., and is therefore used for annealing and for carbonising boxes, for retorts and conveyor chains employed at high temperatures. The outer protection tubes of pyrometers have been made of nichrome, and have lasted for 4000 hours. Nichrome has also been used for crucibles destined to hold up to 176 lb. of metal. Brass, copper, and phosphor copper have been successfully melted in them, no alloying of the nichrome with the crucible content being observed.

Nichrome is also very resistant to the action of acids and of chemicals
generally. It is thus particularly suitable for pickling-baskets. It admits of being readily machined, and possesses a tensile strength approximately double that of cast iron, whilst it equals that metal in hardness.\(^1\)

An acid-resisting alloy known as *illium* contains Ni 60-65, Cu 6-42, Cr 21-07, Mo 4-67, W 2-13, with traces of aluminium, silicon, iron, and manganese. It melts at 1800° C., and has a tensile strength of 50,000 lb. per square inch. It is remarkably resistant to corrosion, a 25 per cent. solution of nitric acid having no apparent influence upon it in twenty-four hours.\(^2\)

In the manufacture of special steels the following alloys are used:

- **Tungsten-nickel** containing 28 to 50 % Ni and 77 to 50 % W
- **Molybdenum-nickel** , 20 to 50 % Mo
- **Chromium-nickel** , 28 to 25 % Cr

In the following table references are given to original papers dealing with other and less important alloys of nickel:

<table>
<thead>
<tr>
<th>Elements alloying with Nickel</th>
<th>Remarks</th>
<th>Alloys studied by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium and copper</td>
<td>No compound. Aluminium renders the alloys very brittle.</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>See p. 129.</td>
<td></td>
</tr>
<tr>
<td>Bismuth</td>
<td>Evidence of NiBi and NiBi(_2).</td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td>NiCd(_4) obtained.</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>No compound. With 10 per cent. chromium the alloy is very resistant to acid attack, especially nitric acid.</td>
<td>Haines, <em>J. Ind. Eng. Chem.</em>, 1910, 2, 397.</td>
</tr>
</tbody>
</table>

\(^1\) See *Iron Age*, 1917, 100, 256; *Met. Chem. Eng.*, 1916, 15, 159.

<table>
<thead>
<tr>
<th>Elements alloying with Nickel.</th>
<th>Remarks.</th>
<th>Alloys studied by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt and copper .</td>
<td>Ternary compounds are not formed. The alloys are hardest which contain nickel and cobalt in equal proportions. All are attacked by nitric acid, but are fairly resistant to sulphuric acid.</td>
<td>Waeblert, Chem. Zentr., 1914, ii, 919, from Oesterl. Zeitsch. Berg- und Hutten- wesen, 1914, 62, 341, 357, 374, 392, 406.</td>
</tr>
<tr>
<td>Copper .</td>
<td>No compound is formed. The freezing-point curve falls regularly from m.p. of Ni to that of Cu, indicating a continuous series of mixed crystals.</td>
<td>Heycock and Neville, Phil. Trans., 1897, 189, 69.</td>
</tr>
<tr>
<td>Copper and chromium</td>
<td>—</td>
<td>Gautier, Compt. rend., 1896, 123, 172.</td>
</tr>
<tr>
<td>Copper, gold, and silver</td>
<td>—</td>
<td>Kurnakoff and Zemczuzny, ibid., 1907, 54, 151.</td>
</tr>
<tr>
<td>Copper, iron, and manganese</td>
<td>—</td>
<td>Vigouroux, Compt. rend., 1909, 149, 1378.</td>
</tr>
<tr>
<td>Copper and manganese</td>
<td>—</td>
<td>Gordon and D. P. Smith, J. Physical Chem., 1918, 22, 194.</td>
</tr>
<tr>
<td>Copper and palladium</td>
<td>—</td>
<td>McFarland and Harder, J. Soc. Chem. Ind., 1915, 34, 1097.</td>
</tr>
<tr>
<td>Copper and silver .</td>
<td>—</td>
<td>DeCesaris, Gazzetta, 1914, 44, 1, 27.</td>
</tr>
<tr>
<td>Copper and zinc .</td>
<td>—</td>
<td>Paravano, ibid., 1914, 44, ii, 279.</td>
</tr>
<tr>
<td>Gold and silver .</td>
<td>—</td>
<td>Paravano and Mazzetti, ibid., 1914, 44, ii, 375.</td>
</tr>
<tr>
<td>Iron .</td>
<td>See this volume, Part II No compounds and no solid solutions.</td>
<td>Parravano, ibid., 1912, 42, ii, 385.</td>
</tr>
<tr>
<td>Manganese .</td>
<td>Compound MnNi appears to be formed in two modifications, stable and unstable.</td>
<td>V. E. Tafel, Metallurgie, 1908, 5, 413.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Guillet, Revue Métallurgie, 1913, 10, 1130; Compt. rend., 1912, 155, 1812.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Huchett, Phil. Trans., 1803, p. 43.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>De Cesaris, Gazzetta, 1913, 43, ii, 609.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Voss, loc. cit.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Portevin, Revue Métallurgie, 1907, 4, 514.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Voss, loc. cit.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dourdine, Revue Métallurgie, 1915, 12, 125. Contrast</td>
</tr>
</tbody>
</table>
### COMPOUNDS OF NICKEL

**General Properties of Compounds of Nickel.**—Nickel usually behaves as a divalent element. Its salts when anhydrous are yellow in colour. They can usually be obtained in various stages of hydration, in which condition they are usually green, and frequently yield series of double salts, analogous in physical properties and in chemical constitution to many double salts obtainable with divalent iron. Like copper salts, those of nickel readily unite with ammonia. Like ferrous salts they absorb nitric oxide, but without change of colour.\(^1\)

Evidence has been obtained of the existence of highly unstable salts of trivalent nickel,\(^2\) but it has not been found possible to isolate them from their solutions.

---


\(^2\) Tubandt, *Zeitsch. anorg. Chem.*, 1905, 45, 73.

<table>
<thead>
<tr>
<th>Elements alloying with Nickel</th>
<th>Remarks</th>
<th>Alloys studied by</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium . .</td>
<td>See Palladium.</td>
<td></td>
</tr>
<tr>
<td>Silicon . .</td>
<td>See p. 133.</td>
<td></td>
</tr>
<tr>
<td>Silver . .</td>
<td>Soluble in nickel to extent of 4 per cent., the m.pt. of the latter being thereby lowered 20° C. On solidification homogeneous mixed crystals separate.</td>
<td></td>
</tr>
<tr>
<td>Thallium .</td>
<td>Nickel retains in solid solution up to about 3 per cent. of thallium.</td>
<td></td>
</tr>
<tr>
<td>Thorium . .</td>
<td>Compound Th(_2)Ni.</td>
<td></td>
</tr>
<tr>
<td>Tin . .</td>
<td>Evidence of formation of NiSn, Ni(_3)Sn(_2), Ni(_4)Sn, and Ni(_4)Sn.</td>
<td></td>
</tr>
<tr>
<td>Tungsten . .</td>
<td>Tungsten increases electrical resistance and incorrodibility.</td>
<td></td>
</tr>
<tr>
<td>Vanadium . .</td>
<td>Vanadium and nickel are miscible in liquid state in all proportions up to 36 per cent. V.</td>
<td></td>
</tr>
<tr>
<td>Zinc . .</td>
<td>NiZn(_3), NiZn(_4), and Ni(_5)Sn obtained.</td>
<td></td>
</tr>
</tbody>
</table>

---
Nickel salts are antiseptic; they arrest fermentation and the growth of plants. The carbonyl is intensely poisonous.

**Preparation of Nickel Salts free from Cobalt.**—As has already been mentioned, nickel closely resembles cobalt in many of its properties, and for many purposes it is quite unnecessary to effect a complete separation of the metals. When, however, pure salts of either metal are required, several convenient methods are at hand for effecting the removal of the unwanted element. In order to remove small quantities of cobalt from nickel salts any of the methods suggested for the removal of nickel from cobalt salts may be utilised. Of these, Fischer's nitrite process is specially convenient.

Another method consists in adding ammonia to the impure bromide in aqueous solution, whereby nickel bromide hexammoniate, NiBr₂·6NH₃, separates out in beautiful violet crystals. Since cobalt does not yield a similar derivative under like conditions, a very pure salt of nickel may be obtained in this way. The hexammoniate of nickel chloride, namely, NiCl₂·6NH₃, may similarly be used.

**NICKEL AND THE HALOGENS**

**Nickelous Fluoride or Nickel Fluoride, NiF₂.**—When anhydrous nickelous chloride is heated with an excess of ammonium fluoride to the point of fusion, *nickel ammonium fluoride* is produced, of formula NiF₂·2NH₄F. This is a yellow, amorphous powder, soluble in water. When heated in a current of an inert gas it yields amorphous nickelous fluoride, the ammonium fluoride being volatilised. The nickel fluoride is yellow, and almost insoluble in water. When heated to 1200–1300 °C. in hydrogen fluoride it is converted into green prisms, which are almost insoluble in water, quite insoluble in ether and in alcohol, and of density 4.63. When heated in air, nickelous fluoride yields the oxide; with sulphur, the sulphide; whilst hydrogen reduces it to metallic nickel. When heated with potassium hydrogen fluoride, a double salt, *nickel potassium fluoride*, NiF₂·KF, is obtained in green plates of density 3.27.

The *trihydrate*, NiF₂·3H₂O, is obtained as bluish green crystals by dissolving either the anhydrous salt in water, or nickelous hydroxide or carbonate in aqueous hydrogen fluoride and concentrating. Boiling water decomposes it with the formation of a pale green oxyfluoride, insoluble in water.

A *dihydrate*, NiF₂·2H₂O, has also been described as a green crystalline salt soluble in water.

A crystalline acid salt, NiF₂·5HF·6H₂O, and an ammonia derivative, 5NiF₂·6NH₃·8H₂O, have been described. Other derivatives and double salts are known.

2 See pp. 43 and 112.
3 Poulenc, *Compt. rend.*, 1892, 114, 1426.
Nickelic Fluoride has not as yet been prepared, and appears to be incapable of separate existence.

Nickelous Chloride or Nickel Dichloride, NiCl₂, is prepared in the anhydrous condition by heating the finely divided metal in dry chlorine. It may also be obtained by evaporating to dryness a solution of nickel oxide (or carbonate) in aqueous hydrogen chloride, and heating gently the solid residue in the absence of air, most advantageously in dry hydrogen chloride gas. The salt sublimes as golden scales of density 2·563.

When heated in air nickel chloride decomposes, evolving chlorine and leaving the oxide. At dull red heat in dry hydrogen a volatile compound, possibly NiClH, is produced. Upon exposure to air the scales absorb moisture and then become easily soluble in water. From such solutions the hexahydrated salt, NiCl₂.6H₂O, is obtained upon evaporation. When exposed to ammonia the anhydrous salt swells to a white powder of formula NiCl₂.6NH₃, readily soluble in water. A substance of similar empirical composition may be obtained as blue octahedra by dissolving nickel chloride in concentrated ammonia, and either allowing to cool or by addition of alcohol. It evolves ammonia upon exposure to air, and particularly in vacuo.

Nickel chloride is also soluble in alcohol.

Several hydrates are known. The monohydrate, NiCl₂.H₂O, is obtained as a yellowish green salt on adding hydrochloric acid to a solution of the chloride in water. The dihydrate, NiCl₂.2H₂O, results upon keeping the hexahydrate in a desiccator. It is yellow in colour.

The usual form of the salt is the hexahydrate, NiCl₂.6H₂O, which may most easily be obtained by dissolving one of the oxides or the carbonate of nickel in hydrochloric acid and crystallising out. It yields monoclinic prisms isomorphous with the corresponding cobalt salt. It is deliquescent, and soluble both in water and alcohol.

The solubility of nickel chloride in water is as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Grams NiCl₂ per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
</tr>
</tbody>
</table>

When exposed to hydrogen under a pressure of 100 atmospheres at 250°C, a fifth normal solution of nickel chloride deposits a little metallic nickel.

Double Chlorides.—Nickel chlorides unite with the chlorides of many other metals, particularly the alkali metals and ammonium, to form double salts. Chief amongst these are nickel ammonium chloride, NH₄Cl.NiCl₂.6H₂O, which occurs as green, monoclinic crystals. Nickel lithium chloride, LiCl.NiCl₂.6H₂O, yields deliquescent, golden prisms.
Monocasium and dicasium nickel chlorides, CsCl.NiCl₂ and 2CsCl.NiCl₂, respectively, have been prepared, and a yellow dirubidium nickel chloride, 2RbCl.NiCl₂. Other double chlorides are known, but their importance is small.

Nickelous Bromide or Nickel Dibromide, NiBr₂, may be obtained in the anhydrous condition by heating the finely divided metal in bromine vapour and subliming the product at bright red heat in the absence of air. A mixture of nitrogen and hydrogen bromide is particularly suitable. It may also be produced by addition of the calculated quantity of dry bromine to finely divided nickel in ether. A yellow salt of composition corresponding to the formula NiBr₂.(C₂H₅)₂O results, and this on heating yields the ether-free, anhydrous bromide. The salt usually occurs as golden scales which absorb moisture on exposure to air. The colour, however, varies according to the state of aggregation of the salt from yellow to dark bronze brown. At red heat in the presence of traces of air or moisture some nickelous oxide is formed, but Richards and Cushman could find no evidence of the existence of an oxybromide under such conditions.

The sublimed salt is slowly soluble in hot water, yielding a clear solution, which may be boiled without decomposition. Berthelot states that the solution on standing in air deposits nickel monoxide. This, however, is not the case with the pure substance. The density of the sublimed salt is 4.64 at 28° C.

The trihydrate, NiBr₂.3H₂O, may be obtained by introducing finely divided nickel into bromine under water, or by dissolving nickel monoxide in aqueous hydrogen bromide. On concentrating the solution, the salt crystallises out in the form of deliquescent needles.

The solubility of nickel bromide in water is as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>NiBr₂ grams solution</th>
<th>58.0</th>
<th>55.0</th>
<th>56.7</th>
<th>59.1</th>
<th>60.4</th>
<th>60.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The hexahydrate, NiBr₂.6H₂O, has been prepared. It melts at 28.5° C., and from the liquid the trihydrate crystallises out. The nonahydrate, NiBr₂.9H₂O, melting at —2.5° C. without decomposition, has also been isolated.

When ammonia is added to a solution of nickel bromide, beautiful violet crystals of the hexammoniate, NiBr₂.6NH₃, separate out. These are soluble in concentrated hot ammonium hydroxide, but insoluble in the cold. On boiling with excess of water, nickel dihydroxide is produced. Since cobalt does not yield a similar derivative, the formation of nickel hexammoniate forms a useful method of separating nickel from cobalt.

Nickelous Iodide or Nickel Di-iodide, NiI₂, may be obtained by heating reduced nickel with iodine, or by dissolving the hydroxide in

1 Campbell, Amer. J. Sc., 1894, 48, 418.
2 Godeffroy, Ber., 1875, 8, 9.
4 Richards and Cushman, Chem. News, 1897, 76, 284, 293.
5 Ducelliez and Raynaud, Compt. rend., 1914, 158, 2002.
aqueous hydrogen iodide, evaporating to dryness and subliming in the absence of air. It forms iron-black scales.\(^1\) With ammonia an ammoniate is produced, which is pale yellow in colour. Blue octahedral crystals of the hexa-ammoniate, \(\text{NiI}_2.6\text{NH}_3\), result when excess of ammonia is added to a solution of the iodide. This loses ammonia on exposure to air, becoming green and ultimately brown.\(^2\)

The hexahydrate, \(\text{NiI}_2.6\text{H}_2\text{O}\), may be obtained by crystallisation from concentrated aqueous solutions. It is bluish green in colour, crystalline but hygroscopic. Its solubility in water is as follows:\(^3\):

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Grams (\text{NiI}_2) per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.4</td>
</tr>
<tr>
<td>10</td>
<td>57.5</td>
</tr>
<tr>
<td>20</td>
<td>59.7</td>
</tr>
<tr>
<td>40</td>
<td>63.5</td>
</tr>
<tr>
<td>60</td>
<td>64.8</td>
</tr>
<tr>
<td>80</td>
<td>65.2</td>
</tr>
<tr>
<td>100</td>
<td>65.3</td>
</tr>
</tbody>
</table>

The solution absorbs iodine, yielding a brown liquid containing probably a periodide.

**OXY-HALOGEN DERIVATIVES OF NICKEL**

**Nickel Chlorate**, \(\text{Ni(ClO}_3\text{)}_2\), may be obtained by double decomposition of aqueous solutions of nickel sulphate and barium chlorate.\(^4\) On concentration rhombic\(^5\) crystals of the hexahydrate, \(\text{Ni(ClO}_3\text{)}_2.6\text{H}_2\text{O}\), are obtained, which at 39 °C. are converted into the tetrahydrate, \(\text{Ni(ClO}_3\text{)}_2.4\text{H}_2\text{O}\). This latter salt melts at about 80 °C., but the existence of a dihydrate in the melt, corresponding to the analogous cobalt derivative, has not been ascertained. The solubility of the salt in water is as follows:\(^5\):

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Grams (\text{Ni(ClO}_3\text{)}_2) in 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>52.66</td>
</tr>
<tr>
<td>10</td>
<td>56.74</td>
</tr>
<tr>
<td>40</td>
<td>64.47</td>
</tr>
<tr>
<td>55</td>
<td>67.60</td>
</tr>
<tr>
<td>65</td>
<td>68.78</td>
</tr>
<tr>
<td>79.5</td>
<td>69.05</td>
</tr>
<tr>
<td>Solid phase</td>
<td>(\text{Ni(ClO}_3\text{)}_2.6\text{H}_2\text{O})</td>
</tr>
<tr>
<td></td>
<td>(\text{Ni(ClO}_3\text{)}_2.4\text{H}_2\text{O})</td>
</tr>
</tbody>
</table>

**Nickel Perchlorate**, \(\text{Ni(ClO}_4\text{)}_2\), may be obtained by dissolving nickel hydroxide or carbonate in a solution of perchloric acid, expelling the excess of acid at 110 °C., and concentrating to crystallisation.\(^6\) The salt separates out in long, green needles, soluble in water, alcohol, and acetone, but insoluble in chloroform. The salt may be dried by warming in a current of dry air or by prolonged exposure over sulphuric acid. It then has the formula \(\text{Ni(ClO}_4\text{)}_2.5\text{H}_2\text{O}\). The crystals melt at 149 °C., but already at 108 °C. slight decomposition sets in with loss of perchloric acid and production of basic salt. The solution in water gradually undergoes hydrolytic dissociation, nickel hydroxide being precipitated.

If a piece of blotting or filter paper is moistened with a solution of nickel perchlorate and introduced into the tip of a Bunsen flame, a series of small detonations ensues.

At — 21.8 °C. the nonahydrate, \(\text{Ni(ClO}_4\text{)}_2.9\text{H}_2\text{O}\), is formed. Two other hydrates, namely, the hexahydrate, \(\text{Ni(ClO}_4\text{)}_2.6\text{H}_2\text{O}\), and the tetrahydrate, \(\text{Ni(ClO}_4\text{)}_2.4\text{H}_2\text{O}\), have been described, as also the hexammoniate, \(\text{Ni(ClO}_4\text{)}_2.6\text{NH}_3\).\(^7\)

---

The solubility of nickel perchlorate in water is as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>30-7</th>
<th>21-3</th>
<th>0</th>
<th>7-5</th>
<th>18</th>
<th>28</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Ni(ClO₄)₂ in 100 grams of solution</td>
<td>20.505</td>
<td>21.06</td>
<td>23.55</td>
<td>24.32</td>
<td>25.06</td>
<td>25.55</td>
<td>27.02</td>
</tr>
<tr>
<td>Density of solution</td>
<td>—</td>
<td>—</td>
<td>1.5726</td>
<td>1.5755</td>
<td>1.5760</td>
<td>1.5841</td>
<td>1.5936</td>
</tr>
</tbody>
</table>

The anhydrous salt apparently cannot exist since the hydrated salt decomposes on warming before all the water has been expelled.

**Nickel Bromate**, Ni(BrO₃)₂·6H₂O, may be prepared by double decomposition of barium bromate and nickel sulphate solutions. It crystallises in unstable octahedra which are green in colour. From its solution in aqueous ammonia, alcohol precipitates the diammoniate, Ni(BrO₃)₂·2NH₃.

**Nickel Iodate**, Ni(IO₃)₂, discovered by Rammelsberg, is interesting on account of its hydrates. The anhydrous salt is obtained as microscopic yellow needles by heating to 100°C a mixture of nickel nitrate, iodic acid, and nitric acid. It is but slightly soluble in water, the solubility decreasing with rise of temperature.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>30</th>
<th>50</th>
<th>75</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Ni(IO₃)₂ in 100 grams solution</td>
<td>1.135</td>
<td>1.07</td>
<td>1.02</td>
<td>0.988</td>
</tr>
</tbody>
</table>

A monohydrate, Ni(IO₃)₂·H₂O, was obtained by Rammelsberg as a bright green powder by concentrating solutions of nickel sulphate and sodium iodate or a solution of nickel hydroxide in aqueous hydriodic acid. Clarke was unable to find this salt.

The dihydrate, Ni(IO₃)₂·2H₂O, exists in two isomeric forms known respectively as the α and β varieties.

The α-salt is obtained by allowing a mixture of nickel nitrate and iodic acid to stand for several days at 25°C to 30°C, when a crystalline mass is formed. It is but slightly soluble in water.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>18</th>
<th>30</th>
<th>50 (transition temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Ni(IO₃)₂ in 100 grams solution</td>
<td>0.53</td>
<td>0.68</td>
<td>0.86</td>
<td>1.78</td>
</tr>
</tbody>
</table>

At 50°C in the presence of water the α-salt is converted into the β-salt, which crystallises in small prisms which are even less soluble in water. Thus:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>8</th>
<th>18</th>
<th>50</th>
<th>75</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Ni(IO₃)₂ in 100 grams solution</td>
<td>0.52</td>
<td>0.55</td>
<td>0.81</td>
<td>1.03</td>
<td>1.12</td>
</tr>
</tbody>
</table>

The trihydrate, Ni(IO₃)₂·3H₂O, was first described by Ditte, who evaporated slowly a mixed solution of nickel nitrate and an alkaline iodate. The salt crystallises out in green transparent prisms.

The tetrahydrate, Ni(IO₃)₂·4H₂O, separates out as green hexagonal
prisms when a solution of nickel nitrate and sodium iodate is con-
centrated between 0° and 10° C. The solubility of the salt is as follows:

<table>
<thead>
<tr>
<th>Temperature ° C.</th>
<th>Grams Ni(IO₃)₂ in 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.78</td>
</tr>
</tbody>
</table>

The hexahydrate, Ni(IO₃)₂·6H₂O, was prepared by Clarke by dissolving nickel carbonate in aqueous iodic acid and allowing to slowly evaporate. The salt yields small green crystals of density 3.70 at 22° C.

Two Periodates of nickel have been described, namely, the meso salt, Ni₂(IO₃)₂, and the diperiodate, Ni₂IO₄. The former is obtained as a greenish yellow amorphous salt by the action of nickel sulphate on a solution of Na₂H₅IO₆ when, on boiling, the salt separates out as a flocculent precipitate. Ni₂IO₄ occurs as a black crystalline salt obtained by drying at 100° C. the bluish green gelatinous precipitate resulting from mixing solutions of nickel sulphate and K₄L₂O₉.

NICKEL AND OXYGEN

It is possible that Tetra-nickel Suboxide, Ni₄O, is capable of existence, for Sabatier and Espli claim to have prepared it by reduction of nickel monoxide in a current of hydrogen at 155° to 250° C.

Tri-nickel Suboxide, Ni₃O, is believed to exist in solution when nickel cyanide is electrolysed between platinum electrodes.

Nickel Suboxide, Ni₂O, has not as yet been obtained, although the corresponding hydroxide, NiOH, appears to have been prepared.

The velocity curve for the reduction of nickel monoxide by hydrogen in the presence of a dehydrator to remove the evolved water possibly indicates the existence of a suboxide, Ni₃O, but this is not certain.

Nickelous Oxide or Nickel Monoxide, NiO, occurs in nature as the mineral Bunsenite in regular octahedra, of density 6.4. In the laboratory it may be obtained by heating the hydroxide, sesqui-oxide, nitrate, or carbonate, when it results as a green crystalline powder, which, on heating, assumes a deep yellow colour. When nickel is heated in steam to a dull red heat, or in nitric oxide to at least 200° C., nickelous oxide is formed. The oxide may also be prepared by igniting nickel borate and lime at a high temperature, and separated as green crystals by treating the cooled mass with aqueous hydrogen chloride. Its density ranges from 6.6 to 6.8.

Nickelous oxide may be reduced more or less completely to the metallic condition by heating in a current of hydrogen at 220° C., in carbon monoxide at 120° C., and in ammonia above 200° C. Solid

---

1 Meusser, loc. cit.
2 F. W. Clarke, loc. cit.
4 Sabatier and Espli, Compt. rend., 1914, 158, 668; 159, 137. See Berger, ibid. 1914, 158, 1788.
5 Tubandt and Riedel, Zeits. anorg. Chem., 1911, 72, 219.
6 Tschugaev and Chlopin, Compt. rend., 1914, 159, 62.
7 Berger, Compt. rend., 1914, 158, 1788. Sabatier and Espli (loc. cit.), however, regard it as Ni₃O.
8 Sabatier and Senderens, Compt. rend., 1892, 114, 1429.
10 Vorster, Jahresber., 1861, p. 310.
carbon reduces it at 450°C. These temperatures of reduction, however, depend upon the mode of preparation and subsequent chemical history of the oxide. Below 300°C, reduction is not complete, but the product is very active catalytically.¹

When ignited in air, nickelous oxide absorbs oxygen, but loses it again as the temperature is raised. When prepared by ignition of nickel nitrate, the oxide contains occluded oxygen, and nitrogen, the latter gas predominating.²

In the electric furnace it melts and on cooling solidifies to green crystals.³ By repeated heating to 1000°C in excess of potassium chloride, amorphous nickel monoxide yields minute octahedral crystals, light yellowish green in colour, and of density 7.45.⁴ It becomes incandescent in fluorine, and in hydrogen sulphide yields an oxysulphide, 2NiS.NiO. Acids dissolve it, yielding nickel salts.

Nickel oxide unites with oxides of several other metals to yield crystalline substances of varied composition. With alumina a blue aluminate, NiO.Al₂O₃, is obtained by fusing the two oxides together at 900°C, using potassium chloride as a flux. It crystallises in small octahedra or octahedral cubes, and even a small excess of either oxide can be distinguished microscopically. With manganese oxide, series of homogeneous mixed crystals have been obtained in an analogous manner, with compositions ranging from NiO.5MnO to 5NiO.MnO. The crystals are slightly yellowish green in colour, and form octahedra and octahedral cubes.

The oxides of magnesium, zinc, and tin likewise yield interesting mixtures.⁵

**Nickelous Hydroxide, Nickel Dihydroxide**, Ni(OH)₂, is obtained as an apple-green precipitate upon warming aqueous alkali hydroxide with a solution of a nickel salt. The precipitate is not perfectly pure, but contains traces of alkali and of the original acid.⁶ It is very slightly soluble in water,⁷ but readily soluble in ammonium hydroxide, yielding a deep blue solution from which the nickel hydroxide is deposited in crystalline form on boiling.

Nickel hydroxide may also be obtained in the crystalline form by allowing a solution of sodium chloride to stand over mercury with a nickel wire connecting both liquids. The reaction is extremely slow, however.⁸

Nickel hydroxide is formed when a fifth normal solution of nickel nitrate is exposed to hydrogen under a pressure of 100 atmospheres, and when a similar concentration of nickel acetate is exposed to hydrogen under the same pressure at 120°C.⁹

Nickel hydroxide dissolves in ordinary distilled water to the extent of 12.7 mgs. of Ni(OH)₂ per litre at 20°C.¹⁰ It is soluble in acids, yielding nickel salts; when heated, water is evolved, leaving a residue

⁵ Hedvall, *ibid.*, 1918, 103, 249.
⁹ Ipatieff, *Ber.*, 1911, 44, 3452.
of nickel monoxide. It is quite insoluble even in concentrated solutions of potassium or sodium hydroxide, and is less readily oxidised in air than the corresponding cobalt derivative. Its solution in ammonia is a solvent for silk, but not for cotton.

Nickel hydroxide has been obtained in colloidal form by treating a solution of nickel sulphate with one of sodium protalbinate or lysalbinate, and dissolving the precipitate in dilute sodium hydroxide.

**Tri-nickel Tetroxide, Nickelo-nickelic Oxide, Ni₅O₄**, results when nickel chloride is subjected to prolonged heating at 410° C. in moist oxygen. In appearance it is grey and metallic.

The oxide may also be obtained in the dehydrated condition, Ni₅O₅·2H₂O or NiO₂·2NiO·2H₂O, by fusing sodium peroxide with metallic nickel and removing the alkali by thorough washing, when it is formed as dark crystals which dissolve in acids yielding salts of divalent nickel. Density 3.412 at 22° C. On heating to redness nickel monoxide is formed.

**Nickel Sesquioxide, Nickelic Oxide, or Nickelous Nickelite, Ni₅O₃ or NiO·NiO₂**. Frequent references occur in the literature to this oxide, the analogue of ferric and cobaltic oxides. It would appear, however, from the researches of Bellucci, that the substance originally believed to have the above composition is in reality the dioxide, NiO₂, or a mixture of this dioxide with the monoxide (vide infra), and that the sesquioxide has not as yet been obtained. These conclusions were arrived at as the result of studying the action of oxidising agents on nickel sulphate in alkaline solution. It was found that the degree of oxidation depended both on the nature of the oxidising medium and upon the rapidity of oxidation. No arrest was found corresponding to the sesquioxide.

Hofmann and Heindlmaier found that, on burning potassium in nickel vessels exposed to air, black prisms were formed to which they ascribed the formula NiO·NiO₂·K₂O. On washing thoroughly with water, raven-black metallic crystals, of empirical composition Ni₂O₃·H₂O, were left. These readily oxidised organic matter, and the authors suggested the formula NiO·NiO₂·2H₂O. The sodium salt, NiO·2NiO₂·Na₂O, has also been prepared. Upon hydrolysis it yields the same hydrated oxide, Ni₅O₄·2H₂O.

**Nickel Dioxide, NiO₂**—Presumably the substance described as nickel sesquioxide and obtained when nickel nitrate or chlorate is gently heated, or when potassium chlorate is fused with nickel chloride, really consists of the dioxide in intimate association with more or less nickel monoxide, according to circumstances (vide supra).

The existence of nickel dioxide was first indicated by Dufau, who prepared barium nickelite, BaO·2NiO₂, by igniting nickel oxide and barium carbonate in an electric arc. The nickelite resulted as dark-coloured crystals of density 4.8 at 20° C. and attacked by water.

---

1. De Schulten, *Compt. rend.*, 1889, 109, 266.
In the hydrated form, \( \text{NiO}_2 \cdot x\text{H}_2\text{O} \), nickel dioxide is obtained by decomposing an aqueous solution of a nickel salt by warming with sodium or potassium hypochlorite, and by passing chlorine through a suspension of nickelous hydroxide in water.\(^1\) It also results when a neutral solution of nickel sulphate is electrolysed. In the literature it is frequently referred to and described as the hydrated sesquioxide.

The hydrated oxide readily dissolves in acids, yielding nickelous salts. It decomposes hydrochloric acid evolving chlorine, and hydrogen peroxide evolving oxygen, being itself reduced to nickel monoxide.\(^2\) With sulphurous acid the sulphite and dithionate are produced. With sulphuric acid oxygen is liberated, nickel sulphate resulting; with aqueous ammonia nitrogen is evolved. Acetic acid gives at first a brownish yellow colour which rapidly turns green.

The oxide is reduced by hydrogen, carbon monoxide, and by carbon. The reduction in an atmosphere of hydrogen begins at about 190° C.\(^3\) The oxide burns in fluorine, and when heated in hydrogen sulphide yields water and the monosulphide, NiS. Pellini \(\text{vide infra}\) ascribes the following graphical formula to the dioxide:

\[
\text{Ni} \overset{O}{\underset{O}{\|}} \cdot x\text{H}_2\text{O}.
\]

A compound of similar composition has been obtained by the action of hydrogen peroxide upon free nickel hydroxide or upon cooled nickel chloride solution to which potassium hydroxide in alcoholic solution is added.\(^4\) It is a greyish green substance giving all the reactions of hydrogen peroxide, and is quite different from the foregoing isomeride. Pellini suggests that it is a true peroxide, namely:

\[
\text{Ni} \overset{O}{\underset{O}{\|}} \cdot x\text{H}_2\text{O}.
\]

Numerous other substances described as oxides of nickel have been placed on record, and formulae suggested such as \(\text{Ni}_4\text{O}_7\),\(^5\) \(\text{Ni}_5\text{O}_7\),\(^6\) \(\text{Ni}_9\text{O}_{15}\),\(^7\) \(\text{NiO}\),\(^8\) and \(\text{Ni}_3\text{O}_2\cdot \text{H}_2\text{O}\).\(^9\) These are probably not separate chemical entities, but mixtures of nickel, nickelous oxide, and nickel dioxide according to circumstances.

When a dilute solution of a nickel salt is electrolysed at 70° C. in the presence of chromic acid and an alkali pyrophosphate, the \textit{tetroxide}, \(\text{NiO}_4\) is obtained.\(^10\)

\(^1\) Bellucci and Clavari, \textit{Gazzetta}, 1905 14, ii, 234; \textit{Atti R. Accad. Lincei}, 1907, 16, i, 647.
\(^2\) Bailey, \textit{Phil. Mag.}, 1879, 7, 126.
\(^3\) Moissan, \textit{Ann. Chim. Phys.}, 1880, 21, 190.
\(^5\) Wicke, \textit{Jahresber.}, 1895, p. 303.
\(^6\) Schröder, \textit{Chem. Zentr.}, 1890, i, 931.
NICKEL AND SULPHUR

Nickel Subsulphide, NiS₂, is stated to be obtained by heating nickel monosulphide in an electric furnace,¹ and by reduction of nickel sulphate with hydrogen or sulphur at red heat;² but Bornemann,³ from a consideration of the freezing-point curve of nickel sulphides, concludes that the subsulphide is not a separate chemical entity, but a eutectic mixture.⁴

Nickel Monosulphide, NiS, occurs in nature as the mineral millerite. It may be prepared by heating nickel and sulphur together or by the action of hydrogen sulphide on nickel heated to redness. As obtained in either of these ways it is a bronze-yellow mass, insoluble in hydrochloric or sulphuric acid, but soluble in nitric acid and in aqua regia. Its density is 4·60,⁵ and specific heat 0·1248. Heated to redness in hydrogen, the sulphide remains unchanged, but in oxygen a basic sulphate is produced. Chlorine and water vapour attack it but slowly.⁶ The sulphide is also obtained as a grey amorphous mass by treating a solution of nickel sulphate at 80° C. with hydrogen sulphide under pressure.⁷

It has been prepared in the crystalline form similar to the mineral by heating solutions of potassium sulphide and nickel chloride to 160–180° C. in a sealed tube.⁸ Ammonium thiocyanate and nickel chloride solutions under similar conditions produce the same sulphide.⁹ Nickel sulphide may also be obtained by precipitation from solutions of nickel salts. It then occurs in three different polymeric forms, α, β, and γ, according to circumstances.¹⁰ Of these, α-nickel sulphide is soluble in dilute mineral acids, even with as low a concentration as 0·01 normal. β-nickel sulphide dissolves easily in 2-normal hydrogen chloride, whilst γ-nickel sulphide is insoluble unless oxidising agents are present.

When dilute reagents are used—for example, nickel sulphate and ammonium sulphide in dilute aqueous solution—probably the α compound is first formed, and then, when the solubility of this substance is exceeded, a precipitate separates out which subsequently more or less completely polymerises to the β and γ forms. This suffices to explain the well-known fact in qualitative analysis that whilst nickel sulphide cannot be precipitated in acid solution by hydrogen sulphide, yet when once precipitated in alkaline solution it is very difficult to dissolve again completely in dilute mineral acid.¹¹

¹ Mourlot, Compt. rend., 1897, 124, 768.
³ Bornemann, Metallurgie, 1908, 5, 13.
⁴ Tschugaev and Chlopin (Compt. rend., 1914, 159, 62) claim to have obtained the subsulphide by a wet method.
⁷ Fouqué and M. Levy, Synthése des minéraux et des roches. Quoted by Moissan, Traité de chimie minérale, 1905, 4, 276.
¹¹ See Baubigny, Compt. rend., 1882, 94, 961, 1183, 1251, 1417, 1473, 1715.
The three varieties of nickel sulphide can be obtained in more or less pure forms separately as follow:

When dilute solutions of nickel sulphate and an alkali sulphide are slowly mixed at the ordinary temperature in the absence of air, 85 per cent. of the precipitate consists of \(\alpha\)-NiS. This sulphide is stable in the absence of air if kept in contact with pure water. In contact with solutions that dissolve it to a slight extent it yields the \(\beta\) and \(\gamma\) varieties. \(\beta\)-nickel sulphide results, mixed with a little \(\gamma\), when a solution of nickel acetate acidified with acetic acid is treated with hydrogen sulphide. Boiling with acetic acid converts it into the \(\gamma\)-form. It appears to be crystalline. \(\gamma\)-nickel sulphide may be obtained in a pure crystalline condition by boiling the mixed sulphides with 2-normal hydrochloric acid.

**Nickel Sesquisulphide,** Ni\(_3\)S\(_2\).—A substance of this composition may be obtained by acting on nickel carbonyl with a solution of sulphur in carbon disulphide.\(^1\)

No indication of the existence of this compound has been obtained by Bornemann\(^2\) in studying the freezing-point curve of the system nickel—sulphur.

**Tri-nickel Tetrasulphide,** Ni\(_5\)S\(_4\), results when metallic nickel is heated either with sulphurous acid or a solution of nickel sulphite to 200° C. under pressure.\(^3\) Its existence as a separate chemical entity is indicated by the shape of the freezing-point curves of nickel sulphides.\(^4\)

**Nickel Disulphide,** NiS\(_2\), is stated to result\(^5\) on fusing nickel carbonate with sulphur and potassium carbonate, and washing the resulting product. Chlorine converts it into the dichloride.

**Nickel Tetrasulphide,** NiS\(_4\), is stated\(^6\) to result when sodium polysulphide saturated with sulphur is allowed to act on a solution of a nickel salt.

From the freezing-point curves of nickel sulphides the existence of two other sulphides has been inferred, namely, Ni\(_2\)S\(_2\) and Ni\(_6\)S\(_5\).\(^7\)

Double sulphides of iron and nickel are present in nickel matte, and are hence of commercial importance. Double sulphides with potassium, K\(_2\)S.3NiS, and barium, BaS.4NiS, may be obtained by fusing nickel, sulphur, and an alkali at a high temperature.\(^8\) They are crystalline compounds. Cobalt yields only the sesquisulphide, Co\(_2\)S\(_3\), in like circumstances. Nickel thus resembles palladium and platinum, whilst cobalt resembles rhodium and iridium in these respects. The position of nickel after cobalt in the Periodic Table thus receives further justification.

**Nickel Sulphite,** NiSO\(_3\), may be prepared in two stages of hydration. The *hexahydrate*,\(^9\) NiSO\(_3\).6H\(_2\)O, crystallises in tetrahedra on evaporating a solution of monoxide in aqueous sulphuric acid in the cold over sulphuric acid. If, on the other hand, the solution is concen-

---

6. Terrell, *Compt. rend.*, 1876, 82, 1116.
trated on the water-bath, the tetrahydrate, $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$, separates out as a green crystalline mass.

The salt readily oxidises in solution. It dissolves in ammonia, yielding a blue crystalline hydrated triammoniate, $\text{NiSO}_4 \cdot 8\text{H}_2\text{O} \cdot 3\text{NH}_3$. A basic sulphite is obtained by addition of sodium sulphite to a solution of a nickel salt, and warming. With ammonium sulphite a green, crystalline precipitate of Nickel Ammonium Sulphite, $\left(\text{NH}_4\right)_2\text{SO}_3 \cdot 2\text{NiSO}_4 \cdot 18\text{H}_2\text{O}$, is obtained.

Nickel Thiosulphate, $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, is readily obtained by mixing equivalent solutions of nickel sulphate and strontium thiosulphate. Insoluble strontium sulphate is filtered off, and the clear solution upon evaporation yields green triclinic prisms of nickel thiosulphate.

Stable in air at ordinary temperatures, the salt decomposes at 100° C. With ammonia it yields two ammoniates, namely, $\text{NiS}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \cdot 4\text{NH}_3$ and $\text{NiS}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \cdot 6\text{NH}_3$.

Nickel Dithionate, $\text{NiS}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$, may be prepared by double decomposition of barium dithionate and nickel sulphate solutions. On concentration of the filtered solution, green triclinic prisms separate out. From its solution ammonia precipitates the hexammoniate, $\text{NiS}_2\text{O}_6 \cdot 6\text{NH}_3$.

Nickelous Sulphate or Nickel Sulphate, $\text{NiSO}_4$, has been obtained in various stages of hydration. Its solution is prepared by dissolving the hydroxide or carbonate in dilute sulphuric acid. When crystallised at 15–20° C., the heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, is obtained as green rhombic prisms, isomorphous with the corresponding ferrous and zinc sulphates. Its density is 1.877, and specific heat 0.341.

Owing to its resemblance to ferrous sulphate or green vitriol it is frequently known as nickel vitriol. It is found in nature as the mineral moresonite. It effloresces in air, yielding the hexahydrate. At 100° C. it loses 4 molecules of water, and at 250° C. becomes anhydrous.

Its solution, evaporated at 50° to 60° C, or allowed to stand after addition of excess of dilute sulphuric acid, deposits crystals of the hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. These are blue, tetragonal pyramids. The same hydrate is produced by prolonged exposure of the heptahydrate to air. This is an example of simple efflorescence, and is not dependent upon sunlight as was once supposed. If the crystals of heptahydrate occupy only a small portion of the containing vessel, they lose water with the formation of the hexahydrate, whether they are exposed to light or not. On the other hand, they are not changed, even by strong light, if the surrounding air is saturated with water vapour, or if the crystals are in contact with filter-paper moistened with turpentine, or if they completely fill the vessel containing them. The hexahydrate is also produced by prolonged exposure of the anhydrous salt to moist

1 Muspratt, loc. cit., Röhrig, loc. cit.
3 Berglund, Bull. Soc. chim., 1874, 21, 212.
5 Vortmann and Padberg, Jahresb., 1889, p. 574.
7 Thorpe and Watts gave 1.949, and Schiff gave 1.931 for the density of the recrystallised heptahydrate.
10 Phillips and Cooper, Pogg. Annalen, 1826, 6, 194.
air (vide infra). The hexahydrate may further be obtained by leaving the heptahydrate for some hours in contact with its saturated solution at 92° to 135° C. The salt is dimorphous. At temperatures above 54° C. both the heptahydrate and the blue hexahydrate are rapidly converted into green monoclinic crystals containing 6 molecules of water.

The tetrahydrate, NiSO₄·4H₂O, has been prepared by crystallisation from a solution of the hexahydrate in sulphuric acid of density 1·4.

The dihydrate, NiSO₄·2H₂O, is formed from solutions by evaporation at temperatures above 118° C. It may also be obtained by the action of concentrated sulphuric acid upon the hepta- or hexa-hydrate. On heating the hexahydrate to 100° C., 5 molecules of water are expelled, the monohydrate, NiSO₄·H₂O, being produced. The same hydrate results when concentrated sulphuric acid is added to a solution of nickel sulphate, being precipitated from solution, and when a twice-normal solution of nickel sulphate is heated to 100° C. under a pressure of 100 atmospheres of air or nitrogen. At 280° C. the hydrated salts yield anhydrous nickel sulphate, which is yellow in colour. It absorbs moisture slowly from the air, yielding ultimately the hexahydrate, and in contact with water rehydrates itself, passing into solution if sufficient water is present. Density 3·643, specific heat 0·216. Heated to redness in it yields nickel monoxide. Heated in a tube open at both ends it begins to decompose at 708° C. to the monoxide. Carbon reduces it to the free metal. A fifth-normal solution of nickel sulphate deposits metallic nickel at 186° C. under a pressure of 100 atmospheres of hydrogen.

It readily absorbs ammonia gas, yielding the hexammoniate, NiSO₄·6NH₃. If the anhydrous salt is dissolved in concentrated aqueous ammonia, however, a dihydrated tetrammoniate is produced, namely, NiSO₄·4NH₃·2H₂O, which separates out in dark blue tetragonal prisms which are unstable in moist air.

The solubility of nickel sulphate in water at various temperatures is as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>9</th>
<th>22·6</th>
<th>30</th>
<th>34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams NiSO₄ in 100 grams water</td>
<td>27·22</td>
<td>31·55</td>
<td>37·90</td>
<td>42·46</td>
<td>45·5</td>
</tr>
<tr>
<td>Solid phase</td>
<td>NiSO₄·7H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature °C</td>
<td>32·3</td>
<td>44·7</td>
<td>53·0</td>
<td>54·5</td>
<td>70</td>
</tr>
<tr>
<td>Grams NiSO₄ in 100 grams water</td>
<td>43·57</td>
<td>48·05</td>
<td>52·34</td>
<td>52·50</td>
<td>59·44</td>
</tr>
<tr>
<td>Solid phase</td>
<td>NiSO₄·6H₂O blue</td>
<td>NiSO₄·6H₂O green</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---


3 De Bruyn, Rec. Trav. chim., 1903, 22, 407.

4 Etard, Compt. rend., 1878, 87, 602.

5 Lesueur, Chem. Zentr., 1895, i, 525.

6 Ipatieff, Ber., 1911, 44, 3452.


9 Erdmann, J. prakt. Chem., 1836, 7, 249; Kane, Annalen, 1838, 26, 199.

10 Steele and Johnson, loc. cit.
The transition points are as follow:

Heptahydrate ⇌ Blue hexahydrate + saturated solution [31.5°C.]
Blue hexahydrate ⇌ Green hexahydrate [58.3°C.]
Green hexahydrate ⇌ Dihydrate + saturated solution [uncertain]

Several basic nickel sulphates have been described, but these are of less interest and importance.\(^1\)

Nickel sulphate yields numerous double salts. Of these the most important is nickel ammonium sulphate, \((\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}\), which is largely used in electroplating. It is readily prepared by adding the requisite quantity of ammonium sulphate to a concentrated solution of nickel sulphate in dilute sulphuric acid. It crystallises in bluish green monoclinic prisms. These are less soluble than the corresponding cobalt salt.

Temperature °C. . . . 3.5 10 16 20 30 40 50 68 85
Grains of salt in 100 grams water . . . 1.8 3.2 5.8 5.9 8.3 11.5 14.4 18.8 23.6

The corresponding potassium,\(^3\) rubidium, and caesium salts have been prepared, and their crystallographic constants determined.\(^4\)

Anhydrous nickel ammonium sulphate, \(3\text{NiSO}_4 \cdot 2(\text{NH}_4)_2\text{SO}_4\), has been prepared by fusing together\(^5\) nickel sulphate, oxide, hydroxide, or carbonate and excess of ammonium sulphate. It combines with water evolving heat. When ignited, anhydrous nickel sulphate remains behind.

Nickel sulphate does not appear to be capable of a separate existence.\(^6\)

NICKEL AND SELENIUM

Nickel subselelde,\(^7\) \(\text{Ni}_2\text{Se}\), is obtained as a golden yellow compound by the prolonged action of hydrogen upon the higher selenides.

Nickel monoselenide or nickel selenide, \(\text{NiSe}\), results in regular double tetrahedra when nickel is exposed at dull red heat to vaporised selenium diluted with nitrogen. It is also obtained by the action of hydrogen selenide upon anhydrous nickel chloride at bright red heat.\(^7\) It is greyish blue in colour. Density 8.46.

Nickel sesquiselenide, \(\text{Ni}_2\text{Se}_3\), is obtained by exposing anhydrous nickel chloride to hydrogen selenide at dull red heat. Nickelo-nickelic selenide, \(\text{Ni}_3\text{Se}_4\), is obtained in the same way as a grey product apparently crystallising in the cubic system. The diselenium, \(\text{NiSe}_2\), is a dark grey compound obtained by heating anhydrous nickel chloride in hydrogen selenide at 300°C.\(^7\)

Nickel selenite, \(\text{NiSeO}_3\), has been prepared in several stages of

---

\(^1\) Marshall, Analyst, 1899, 24, 202; de Clermont, Compt. rend., 1893, 117, 229; Athanasseso, ibid., 1886, 103, 271.
\(^3\) Tobler, Annalen, 1855, 95, 193; von Hauer, J. prakt. Chem., 1868, 103, 114.
\(^4\) Tutton, Trans. Chem. Soc., 1893, 63, 337; Phil. Trans., 1915, 1, 216, 1.
\(^5\) Laclaud and Lepierre, Bull. Soc. chim., 1892, 7, 600; Compt. rend., 1892, 115, 115.
\(^7\) Fonzes-Diacon, Compt. rend., 1900, 131, 556.
hydration. The *semihydrate*, 2NiSeO₃·H₂O, is obtained as insoluble rhombic prisms by heating a solution of nickel carbonate in selenious acid to 230° C. in sealed tubes.¹ It is stable at 100° C. The *monohydrate*, NiSeO₃·H₂O, is precipitated on addition of an alkali selenite to a solution of a nickel salt. On drying over sulphuric acid it becomes a grey powder.² The *dihydrate*, NiSeO₃·2H₂O, has also been obtained.³

**Nickel Selenate**, NiSeO₄·6H₂O, may be obtained as green octahedral crystals by allowing a solution of nickel carbonate in selenic acid to evaporate slowly at ordinary temperature.⁴ Nickel selenate unites with the selenates of the alkali metals to yield double salts⁸ of the type M₂SeO₄·NiSeO₄·6H₂O. These salts crystallise in holohedral prisms belonging to the monoclinic system, and are isomorphous with the double sulphates of analogous composition, of which ferrous ammonium sulphate is the best known example. The following salts have been carefully studied by Tutton:⁶ *potassium nickel selenate*, K₂SeO₄·NiSeO₄·6H₂O (density at 20° C. 2.559, molecular volume 206·14); and the nickel selenates of rubidium (density 2.856, molecular volume 219·96), caesium (density 3·114, molecular volume 229·17) and ammonium (density 2·243, molecular volume 216·53).

**NICKEL AND TELLURIUM**

**Nickel Sesquitefluride**, Ni₂Te₃, occurs in nature as the mineral *melonite*. It may be prepared by the addition of sodium telluride solution to one of nickel acetate acidulated with acetic acid.⁷ The resulting black precipitate has the composition Ni₂Te₃·4H₂O, and when heated in hydrogen yields *Nickel Monotelluride*, NiTe.

**Nickel Tellurite** may be obtained as a pale greenish yellow precipitate of composition NiTeO₃·2H₂O, by addition of sodium tellurite solution to one of nickel chloride.⁸ When heated it loses water, becoming light brown in colour.

**NICKEL AND CHROMIUM**

Neutral solutions of nickel salts produce with potassium chromate a chocolate-brown precipitate of hydrated basic nickel chromate, NiO·NiCrO₄·Aq. It forms only slowly in the cold, even from concentrated solutions. Boiling hastens the precipitation. The reaction may be utilised in detecting small quantities of nickel.⁹

**Nickel Chromate**, NiCrO₄, is obtained by maintaining a solution of nickel carbonate and chromic acid at 260° C. in a sealed tube for

⁵ Von Hauer, *loc. cit.*
⁸ Weih and Wolesensky, *J. Amer. Chem. Soc.*, 1913, 35, 718. The sodium tellurite is obtained by fusing equimolecular quantities of sodium carbonate and tellurium dioxide. It readily dissolves in water and crystallises with 5 molecules of water, thus Na₄TeO₄·5H₂O.
several hours. It yields black crystals, insoluble in hot dilute nitric acid, and only slowly attacked by concentrated nitric acid or aqua regia. On pouring alcohol into an ammoniacal solution of this salt, the hexammoniate, NiCrO$_4$·6NH$_3$, separates out in dichroic crystals.

**Nickel Dichromate**, 2NiCrO$_4$·3H$_2$O, is obtained by heating an aqueous solution of nickel carbonate and chromic acid to a high temperature. It occurs in reddish brown transparent prisms, which are deliquescent.

**Double Chromates**.—Several double chromates containing nickel have been prepared. Amongst these are potassium nickel chromate,$^3$ K$_2$CrO$_4$·NiCrO$_4$·6H$_2$O, and the corresponding ammonium, rubidium, and caesium salts. Basic chromates have also been described.$^4$

**NICKEL AND MOLYBDENUM**

Alloys of nickel and molybdenum are prepared by direct union of the two metals or by reduction of their mixed oxides in the electric furnace.  

**Nickel Molybdate**, NiMoO$_4$, is prepared by fusing a mixture of sodium molybdate and chloride with nickel chloride. It occurs as green prisms.$^5$ The hydrated ammoniate, NiMoO$_4$·NH$_3$·2H$_2$O, is obtained as greenish blue prisms by dissolving nickel hydroxide in ammoniacal ammonium molybdate.$^6$

Complex nickel-molybdates have been prepared.$^7$

**NICKEL AND NITROGEN**

**Nickel Nitride**, ?Ni$_3$N (or Ni$_2$N$_2$), has been obtained$^8$ by heating reduced nickel in a current of ammonia at about 500$^\circ$ C. It is also formed when nickelamide, Ni(NH$_2$)$_2$, is heated at 120$^\circ$ C. in a vacuum.$^9$ Nickel nitride is a black powder, readily soluble in dilute hydrochloric or sulphuric acid, and completely decomposed when heated in hydrogen, its nitrogen being evolved as ammonia.$^{10}$

**Nickel Azoimide**, Ni(N$_3$)$_2$·H$_2$O, and a **Basic Azoimide**, N$_3$·Ni·OH, have been obtained$^11$ as green explosive crystalline bodies, exploding at 247–271$^\circ$ C. Bright green, explosive potassium nickel azoimide, KN$_3$·Ni(N$_3$)$_2$, has also been prepared.

**Nickelamide**, Ni(NH$_4$)$_2$, is precipitated as a red, flocculent mass when a solution of nickel thiocyanate in liquid ammonia is treated with

---

2 Briggs, *ibid.*, 1907, 56, 246.
10 In no case could Beilby and Henderson induce the nickel to combine with more than 7-5 per cent. of nitrogen; Ni$_3$N requires 7-36 per cent.; Ni$_2$N requires 10-6 per cent. If the latter formula is correct for the nitride, as analogy with iron and cobalt would lead one to anticipate, the substance obtained by Beilby and Henderson was probably a solid solution of nickel in the nitride.
11 Curtius and Rissom, *J. prakt. Chem.*, 1898, [ii], 58, 261; Curtius and Darapsky, *ibid.*, 1900, 61, 418.
an equivalent amount of potassamide solution. It reacts with water, producing nickel hydroxide and ammonia:

\[ \text{Ni(NH}_2\text{)}_2 + 2\text{H}_2\text{O} = \text{Ni(OH)}_2 + 2\text{NH}_3. \]

At 120°C, it yields nickel nitride.\(^1\)

**Nitro-nickel, \(\text{Ni}_2\text{NO}_3\)._** When nitrogen peroxide, suitably diluted with nitrogen, is passed over reduced nickel, a black mass of nitro-nickel is obtained.\(^2\) Water decomposes it vigorously. When heated in a current of nitrogen nitrous fumes are first evolved, then the substance decomposes with violence, leaving a residue of nickel and its oxide.

**Nickel Nitrite, \(\text{Ni(NO}_3\text{)}_2\)._** A solution of nickel nitrite is obtained by double decomposition of nickel sulphate and barium nitrite, but the salt itself has not been isolated. It yields a stable double salt with potassium nitrite, namely, \(4\text{KNO}_2 \cdot \text{Ni(NO}_3\text{)}_2\), which crystallises in brownish red octahedra, when excess of potassium nitrite is added to a concentrated solution of nickel nitrite.\(^3\) In the presence of a calcium salt a yellow crystalline precipitate is obtained, of composition represented by the formula \(2\text{KNO}_2 \cdot \text{Ca(NO}_3\text{)}_2 \cdot 2\text{Ni(NO}_3\text{)}_2 \) or \(\text{K}_4\text{CaNi(NO}_3\text{)}_6\), which closely resembles potassium cobalti-nitrite in appearance. The corresponding barium and strontium salts have been prepared.

**Nickelous Nitrate or Nickel Nitrate, \(\text{Ni(NO}_3\text{)}_2\)._** This salt may be obtained in the anhydrous condition by the action of nitric anhydride or a solution of this in nitric acid upon the hydrated salt.\(^5\) It is a pale greenish yellow powder, which decomposes at 105°C to 110°C, evolving nitrous fumes.

The hexahydrate, \(\text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}\), is dimorphous. It is obtained as green monoclinic crystals by concentration of a solution of nickel hydroxide or carbonate in dilute nitric acid at temperatures below 55°C.—most advantageously at about 40°C. Density \(6\) 2.065 at 14°C. At low temperatures the salt separates out in crystalline lamelle. The crystals deliquesce in moist air and effloresce in the dry. Their solubility in water is as follows: \(^7\)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Grams Ni(NO(_3))(_2) per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44.32</td>
</tr>
<tr>
<td>20</td>
<td>49.06</td>
</tr>
<tr>
<td>41</td>
<td>55.22</td>
</tr>
<tr>
<td>56.7</td>
<td>62.76</td>
</tr>
</tbody>
</table>

The composition of a saturated solution of the hexahydrate in water at temperatures ranging from —21°C to 41°C is given by the expression: \(^7\)

\[ \text{Ni(NO}_3\text{)}_2 + (12.886 - 0.11856\times t)\text{H}_2\text{O}. \]

Crystals of the hexahydrate melt at about 56.7°C, losing 3 molecules of water. If maintained at 70°C they melt, large orthorhombic

---

crystals of the *trihydrate*, \( \text{Ni(NO}_3\text{)}_2 \cdot 3\text{H}_2\text{O} \), being produced. This hydrate is stable between \( c. 55^\circ \text{C} \) and \( 95^\circ \text{C} \), at which latter temperature the crystals melt with simultaneous decomposition.

The solubility of the trihydrate in water is as follows:\(^1\):

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>58</th>
<th>60</th>
<th>64</th>
<th>70</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams ( \text{Ni(NO}_3\text{)}_2 ) per 100 grams solution</td>
<td>61.61</td>
<td>61.99</td>
<td>62.76</td>
<td>63.95</td>
<td>70.16</td>
<td>77.12</td>
</tr>
</tbody>
</table>

At \( 55^\circ \text{C} \) nickel nitrate has nearly the same solubility as the corresponding cobalt salt.

At \( -16^\circ \text{C} \) the *nonahydrate*, \( \text{Ni(NO}_3\text{)}_2 \cdot 9\text{H}_2\text{O} \), can be isolated from the solution, but only with difficulty on account of the low temperature. Its solubility in water is as follows:\(^1\):

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>23</th>
<th>21</th>
<th>10.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams ( \text{Ni(NO}_3\text{)}_2 ) per 100 grams solution</td>
<td>39.02</td>
<td>39.48</td>
<td>44.13</td>
</tr>
</tbody>
</table>

The solubility curve of this hydrate intersects that of the hexahydrate at \( -16^\circ \text{C} \).

When alcohol is added to a solution of nickel nitrate in aqueous ammonia, blue octahedral crystals of the *monohydrated tetrammoniate*, \( \text{Ni(NO}_3\text{)}_2 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O} \), separate out. These are unstable in air.\(^2\)

**Double Nitrates.** — A double nitrate of nickel and bismuth, \( 3\text{Ni(NO}_3\text{)}_2 \cdot 2\text{Bi(NO}_3\text{)}_3 \cdot 24\text{H}_2\text{O} \), has been prepared as green crystals, melting at \( 69^\circ \text{C} \) without decomposition.\(^3\) Other double nitrates are known,\(^4\) including double nitrates of certain rare earth metals,\(^5\) and several basic salts had been prepared.\(^6\)

### NICKEL AND PHOSPHORUS

**Nickel Subphosphide** or **Di-nickel Phosphide**, \( \text{Ni}_2\text{P} \), is obtained in the form of grey needles, of density 6.3, when nickel and phosphorus are heated together in an electric furnace,\(^7\) or when reduced nickel is exposed at dull red heat to vapours of phosphorus trichloride,\(^8\) tribromide, or tri-iodide. Small brilliant yellowish white crystals are obtained by this latter process. Nickel subphosphide also results on reducing the phosphate with hydrogen at high temperatures,\(^9\) and by pouring a suspension of nickel hydroxide into a boiling solution of caustic potash to which phosphorus has been added.\(^10\) A brown precipitate is first formed, but after a few minutes a black residue of \( \text{Ni}_2\text{P} \) or \( \text{Ni}_4\text{P}_2 \) is obtained, which dissolves but slowly in most dilute acids. Towards concentrated nitric acid it behaves like iron, but readily dissolves in dilute nitric acid.

---


\(^3\) Urbain and Lacombe, *Compt. rend.*, 1903, 137, 568.


\(^5\) See this Series, Vol. IV, p. 401.

\(^6\) Rousseau and Tite, *Compt. rend.*, 1892, 141, 1184.

\(^7\) Maronneau, *Compt. rend.*, 1900, 130, 656.


Nickel Sesquiphosphide, Ni\(_2\)P\(_3\), was obtained by Granger \(^1\) by passing phosphorus vapour over nickel at a low red heat. It is non-magnetic, grey, and friable, insoluble in hydrochloric or nitric acid, as also in aqua regia. It is permanent in air up to a dull red heat.

Nickel Diphosphide, NiP\(_2\), is prepared \(^2\) by heating an alloy of nickel and tin, containing 5 per cent. of the former metal, with phosphorus in a sealed tube to a temperature of 700\(^\circ\) C. If the alloy is heated with less than 20 per cent. of its weight of phosphorus the nickel diphosphide may be isolated from the residue by treatment with warm concentrated hydrochloric acid, in which it is insoluble.

The phosphide is a crystalline substance, of metallic appearance, and of density 4·62 at 18\(^\circ\) C.

Nickel Triphosphide, NiP\(_3\), results \(^2\) on heating an alloy of nickel and tin, containing 5 per cent. of nickel, with more than 20 per cent. of its weight of phosphorus in a sealed tube to 700\(^\circ\) C. Tin triphosphide, SnP\(_3\), is simultaneously produced, but may be decomposed by heating the mixture under reduced pressure at 360\(^\circ\) C. Treatment with hydrochloric acid removes the products, leaving the triphosphide as a crystalline residue, of density 4·19 at 18\(^\circ\) C.

The phosphides, Ni\(_5\)P\(_2\) and Ni\(_3\)P\(_3\), have been described.\(^3\) The former of these exists in two modifications, namely, \(\beta\)Ni\(_5\)P\(_2\), which is stable at high temperatures and is transformed at 1025\(^\circ\) C. into \(\alpha\)Ni\(_5\)P\(_2\).

Nickel Hypophosphite, NiH\(_4\)(PO\(_4\))\(_2\)-6H\(_2\)O, may be obtained by double decomposition of nickel sulphate and barium hypophosphite solutions, or by dissolving nickel hydroxide in hypophosphorous acid. From the solution thus obtained the hexahydrated salt crystallises out in green regular octahedra.

On warming the solution to 100\(^\circ\) C. metallic nickel is deposited in consequence of partial decomposition. On raising the moistened crystals to 120\(^\circ\) C. the salt is completely reduced \(^4\)

Nickel Phosphite, Ni\(_2\)(HPO\(_3\))\(_2\)-H\(_2\)O.6H\(_2\)O, may be obtained in an analogous manner to the preceding salt.

Nickel Metaphosphate, Ni(PO\(_3\))\(_2\).—The anhydrous salt is obtained \(^5\) by the action of phosphoric acid on nickel sulphate at 300\(^\circ\) C. It is a yellow substance, insoluble in water and most acids, but attacked by concentrated sulphuric acid. It may be obtained in the crystalline form by melting with metaphosphoric acid.

A polymeride of this salt, namely, Nickel Hexametaphosphate, [Ni(PO\(_3\))\(_2\)]\(_n\), or Ni\(_3\)P\(_6\)O\(_{18}\), is obtained as a green, gelatinous precipitate on addition of the corresponding sodium salt to a concentrated solution of nickel chloride.\(^6\)

Nickel Orthophosphate, Ni\(_3\)(PO\(_4\))\(_2\)-7H\(_2\)O, may be prepared by adding sodium orthophosphate to a solution of a soluble nickel salt.\(^7\) It is pale green in colour, turning to yellow when heated.\(^8\) A double

---

4. Rammelsberg, Ber., 1872, 5, 494.
8. Salvetat (Compt. rend., 1859, 48, 295) has suggested its employment for pigmented purposes.
phosphate of potassium and nickel, namely, $2K_3PO_4\cdot Ni_3(PO_4)_{2s}$ has been isolated.¹

**Nickel Pyrophosphate**, $Ni_2P_2O_7\cdot 6H_2O$, results as a green amorphous powder on adding sodium pyrophosphate solution to one of a nickel salt. It is soluble in excess of the former reagent, in mineral acids, and in aqueous ammonia. It may be obtained in the crystalline form by dissolving in sulphurous acid and reprecipitating by boiling.² The anhydrous salt is obtained by igniting the double ammoniacal orthophosphate. Its density at 25°C is 3.98.³

Several thiophosphates of nickel have been prepared.

**Nickel Thio-orthophosphate**, $Ni_3(PS_4)_{2s}$, is obtained by heating the requisite quantities of anhydrous nickel chloride and phosphorus pentasulphide in a retort ⁴:

$$3NiCl_2 + 2P_2S_5 \rightarrow Ni_3P_2S_8 + 2PSCl_3.$$  

The thiophosphoryl chloride distils over, and the residue is freed from nickel chloride by treatment with hydrochloric acid, washed and dried.

The salt yields brownish black crystalline plates, which ignite on heating in air, evolving sulphur dioxide.

**Nickel Thiopyrophosphate**, $Ni_3P_2S_8$, may be obtained ⁵ by heating nickel for forty hours with sulphur and phosphorus in sealed tubes. It forms brilliant grey hexagonal crystals of density 2·4. They are very resistant to acid attack, even to nitrohydrochloric acid.

**Nickel Thiopyrophosphate**, $Ni_2P_2S_7$, has been obtained in a similar manner to the preceding compound ⁶ by heating for twenty-two hours. It is a deep brown crystalline powder, which is attacked by nitric acid at 150°C.

**NICKEL AND ARSENIC**

Nickel combines with arsenic in several different proportions, yielding arsenides.

**Tri-nickel Diarsenide**, $Ni_3As_{2s}$, is formed by reducing nickel arsenate or a mixture of nickel oxide and arsenious oxide with potassium cyanide,⁷ and also when reduced nickel is heated at 800–1400°C in vaporised arsenic chloride.⁸ It is a grey substance, which melts at 1000°C; density 7·86. It is soluble in acids and fused alkalies.

**Nickel Arsenide**, $NiAs$, is formed by the above method at 400–800°C. It is identical with the mineral *niccolite* or *nickeline*,⁹ and has, like it, a red colour. Density 7·57.

**Nickel Diarsenide**, $NiAs_2$, occurs in nature as *chloanthite* and *Rammelsbergite*. It may be prepared by heating nickel arsenide and arsenic in hydrogen at a decreasing temperature, being formed as a grey powder as the temperature falls below 400°C.¹⁰

---

² Schwarzenberg, *Annalen*, 1848, 65, 158.
⁹ Vigouroux, loc. cit.
Stable Penta-nickel Diarsenide, $\text{Ni}_5\text{As}_2$, has been described.

Nickel Arsenite, $3\text{NiO} \cdot \text{As}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, is obtained as a green precipitate on addition of an alkali arsenite to a solution of a nickel salt.²

Nickel Orthoarsenate, $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, occurs in nature as the mineral Annabergite, found at Annaberg in Saxony. It may be prepared by addition of ammonium arsenate to a nickel salt, the solution being kept neutral. If ammonia is present in excess the molecules of water are partially replaced by ammonia, yielding hydrated ammoniates, which are insoluble in water, but readily soluble in acids and in ammonia. The following ammoniates have been distinguished³:

$$\text{Ni}_3(\text{AsO}_4)_2 \cdot 2\text{NH}_3 \cdot 7\text{H}_2\text{O}, \quad \text{Ni}_3(\text{AsO}_4)_2 \cdot 2\text{NH}_3 \cdot 6\text{H}_2\text{O}, \quad \text{and} \quad \text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{NH}_3 \cdot 5\text{H}_2\text{O}.$$  

NICKEL AND ANTIMONY

Nickel Monantimonide or Nickel Antimonide, $\text{NiSb}$, may be prepared by direct combination of the elements ⁴ or by heating nickel to 800° C. in the vapour of antimony trichloride.⁵ It occurs as reddish violet crystals, which are non-magnetic, and of density 7.70 at 0° C. It fuses at 1100° C. and decomposes at 1400° C. Chlorine and oxygen act on it at red heat, and warm concentrated nitric or sulphuric acid decomposes it.

The freezing-point curve of nickel and antimony indicates the existence of several other antimonides, namely, $\text{Ni}_3\text{Sb}_2$, $\text{Ni}_4\text{Sb}$, and possibly of $\text{Ni}_5\text{Sb}_5$.⁶ $\text{Ni}_5\text{Sb}$ may also exist.⁷

Nickel Antimonate, $\text{NiSb}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$, is obtained by precipitating nickel acetate with a solution of antimonic acid.⁸ The precipitate is a green mass, which becomes darker on desiccation, but yielding a pale green powder. When dried over sulphuric acid it loses three molecules of water, yielding the dihydrate, $\text{NiSb}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$. Another molecule of water is expelled at about 160° C. and the salt becomes anhydrous at about 300° C.

Nickel Thioantimonite, $\text{Ni}_3\text{Sb}_2\text{S}_6$, is obtained by precipitation from a solution of a nickel salt with a dilute solution of potassium thioantimonite.⁹ It is readily oxidised, and always contains potassium if prepared from concentrated solutions.

Nickel Vanadate, $3\text{NiO} \cdot \text{V}_2\text{O}_5$, is obtained by fusing a mixture of vanadic acid, nickel bromide, and a large excess of sodium bromide, and washing the cooled product with dilute nitric acid.¹⁰ The crystals remaining are in the form of green prismatic needles. They do not melt at a bright red heat, and are insoluble in hot nitric acid. Fused potassium carbonate slowly attacks them.

¹ Friedrich and Bennigson, loc. cit.
² Reynoso, Compt. rend., 1850, 31, 68; Girard, übid., 1852, 34, 918; 1853, 36, 793; Reichard, Ber., 1898, 31, 2165.
⁵ Vigouroux, Compt. rend., 1908, 147, 976.
⁶ Lossew, loc. cit.
⁸ Senderens, Bull. Soc. chim., 1899, 21, 47.
⁹ Pouget, Compt. rend., 1899, 123, 104.
¹⁰ A. Ditte, Compt. rend., 1888, 96, 1048.
NICKEL AND ITS COMPOUNDS

NICKEL AND CARBON

Nickel Carbide, Ni₃C, is an endothermic compound, the molecular heat of formation of which is −394 ± 10 cals. It results when metallic nickel and carbon are heated together,¹ the optimum temperature of formation being approximately 2100° C., and the maximum carbon content 6-42 per cent. At lower temperatures dissociation takes place, which is fairly rapid at 1600° C., but much slower at 900° C. Hence in preparing the carbide it is essential to cool rapidly, although even the quenched product contains but little of the carbide. Furthermore the carbide cannot be separated from the dissociated graphite owing to the extreme toughness of the quenched product which refuses to be powdered.

The nickel-carbon system appears to be similar to that of iron and carbon, and an alloy containing 1 per cent. of carbon is so brittle that it can be broken by a hammer. Alloys containing larger quantities of carbon, on the other hand, are tough.²

Nickel Tetracarbonyl, Ni(CO)₄, is obtained when carbon monoxide is passed over metallic nickel in a finely divided condition, such as is obtained by the reduction of nickel oxide in hydrogen at 400° C., the best temperature for obtaining the carbonyl being about 30-50° C. The carbonyl is condensed in a cooled vessel. The reaction may be advantageously carried out under a pressure of 2-100 atmospheres of carbon monoxide, in which case the temperature may be raised even to 250° C. without fear of decomposition. ³

Nickel carbonyl is a colourless liquid, boiling at 48-2° C. and solidifying at −25° C.⁴ Its density is 1-3185 at 17° C.⁵ At 50° C. its vapour density corresponds to the formula Ni(CO)₄ when determined in Victor Meyer's apparatus.⁶ In an atmosphere of carbon monoxide its density is normal up to 100° C., whilst in nitrogen its dissociation is practically complete at 155° C.⁷

Nickel carbonyl reacts slowly with concentrated sulphuric acid, yielding carbon monoxide, hydrogen, and nickel sulphate.⁸

\[ \text{Ni(CO)}_4 + \text{H}_2\text{SO}_4 = \text{NiSO}_4 + \text{H}_2 + 4\text{CO}. \]

Solutions of nickel carbonyl in carbon tetrachloride react with chlorine, bromine, or iodine in similar solution, yielding carbon monoxide and the anhydrous halide.⁹ Thus:

\[ \text{Ni(CO)}_4 + \text{Cl}_2 = \text{NiCl}_2 + 4\text{CO}. \]

Moist air decomposes the carbonyl as does also carbon disulphide.¹⁰

¹ Ruff and W. Martin, Metallurgie, 1912, 9, 143; Ruff, Ber., 1912, 45, 3139; Ruff and Gersten, Ber., 1913, 46, 409; Ruff, Bornmann, and Keilig, Zeitsch. anorg. Chem., 1914, 88, 365; Briner and Senglet, J. Chem. phys., 1915, 13, 351. See also Friedrich and Leroux, Metallurgie, 1910, 7, 10.
² Friedrich and Leroux, loc. cit.
⁶ Mond, Langer, and Quincke, loc. cit.
⁹ This reaction has been fully studied by Dewar and Jones, Trans. Chem. Soc., 1910, 97, 1226.
When inhaled even in small quantities the vapour of nickel carbonyl is very poisonous,\(^1\) being decomposed in the lungs to carbon monoxide and a nickel derivative—possibly the basic carbonate.

**Nickel Carbonate,** \(\text{NiCO}_3.\) When solutions of nickel salts are treated with potassium or sodium carbonate, basic nickel carbonates are precipitated, their compositions varying according to circumstances.\(^2\) The normal hexahydrated carbonate, \(\text{NiCO}_3.6\text{H}_2\text{O},\) is obtained when a solution of sodium hydrogen carbonate saturated with carbon dioxide is added to one of nickel nitrate and allowed to stand at a low temperature. It separates in monoclinic crystals, which lose water on warming. The trihydrate, \(\text{NiCO}_3.3\text{H}_2\text{O},\) is also known.\(^3\) The anhydrous salt results when nickel chloride solution is heated with calcium carbonate to 150° C. It crystallises in pale green rhombohedra. Double carbonates have been prepared.\(^3\)

**Nickel Monocyanide.** Reduction of potassium nickelocyanide, \(K_2\text{Ni(CN)}_4,\) with potassium amalgam yields a red salt, \(K_2\text{Ni(CN)}_2,\) in which nickel appears to be monovalent. Upon acidifying, an orange-yellow precipitate of the monocyamine is obtained, \(\text{NiCN}._2.\) It readily oxidises to nickel cyanide, \(\text{Ni(CN)}_2.\)\(^4\)

**Nickel Cyanide,** \(\text{Ni(CN)}_2._1.\) When potassium cyanide is added to a solution of a nickel salt, a green precipitate of nickel cyanide is produced. This readily dissolves in excess of the reagent, yielding potassium nickelocyanide, \(K_2\text{Ni(CN)}_4.\) Solutions of this salt contain the complex ion \(\text{Ni(CN)}_4,\) so that the above formula is probably more correct than \(2\text{KCN}._\text{Ni(CN)}_2.\)\(^5\) It crystallises with one molecule of water, \(K_2\text{Ni(CN)}_4\cdot\text{H}_2\text{O}.\) Density 1:875 at 11°C, and 1:871 at 14:5° C.\(^6\) It is readily decomposed by the addition of sodium hypobromite, hydrated nickel peroxide being thrown down as a black precipitate (see p. 75). The corresponding cobalt salt is, in like circumstances, oxidised to the stable cobalticyanide which remains in solution. This fact is made use of in separating nickel and cobalt in qualitative analysis. Nickel does not yield stable salts corresponding to the ferro- and ferri-cyanides.

The tetrahydrate, \(\text{Ni(CN)}_2.4\text{H}_2\text{O},\) separates after prolonged standing as steel-blue leaflets from a cold, aqueous solution of nickel sulphate, potassium cyanide, and ammonia.\(^7\)

On prolonged standing the ammoniacal solution of nickel cyanide deposits crystalline needles of the ammoniate, \(2\text{Ni(CN)}_2.2\text{NH}_3\cdot\text{H}_2\text{O}.\) This, at 250° C., is converted into the anhydrous cyanide.\(^8\)

**Nickel Thiocyanate,** \(\text{Ni(CNS)}_2._1.\) has been obtained in the anhydrous condition as a chocolate-coloured amorphous powder.\(^9\) The hydrated salt, \(2\text{Ni(SCN)}_2.3\text{H}_2\text{O},\) obtained by dissolving nickel carbonate in thiocyanic acid is a yellowish brown crystalline powder.\(^10\) Double salts

---

\(^1\) Armit, *J. Hygiene*, 1907, 7, 525.
\(^5\) Rossai, *Gazzetta*, 1915, 45, [i], 6.
\(^7\) K. A. Hofmann and Höchtlens, *Ber.*, 1903, 36, 1149.
\(^9\) Grossmann, *Ber.*, 1904, 37, 559.
with potassium, sodium, and ammonium have been obtained, as have also ammonia derivatives.  

**Nickel Thiocarbonate Hexammoniate**, NiCS₃.3NH₃, is prepared by gently warming nickel hydroxide with aqueous ammonia and carbon disulphide. It crystallises in ruby-red, transparent needles, which are but slightly soluble in water. On warming, carbon disulphide is evolved. Upon exposure to air both ammonia and carbon disulphide escape.

**Nickel, Silicon, and Tin**

Di-nickel Silicide or Nickel Subsilicide, Ni₂Si, is obtained by heating nickel and 10 per cent. of silicon in a carbon crucible in an electric furnace. It is a stable, steel-grey substance, density 7.2 at 17° C. Fluorine attacks it with incandescence at ordinary temperatures, and chlorine at red heat. It dissolves readily in hydrogen fluoride, less so in hydrogen chloride; aqua regia decomposes it completely.

The freezing-point curve of nickel and silicon indicates the existence of several other silicides, namely, Ni₃Si, Ni₅Si₂, NiSi, and Ni₃Si₃. A tetranickel silicide, Ni₄Si, has been isolated. Density curves, however, apparently indicate the existence of three silicides only, namely, Ni₂Si, NiSi, and Ni₃Si₃.

**Nickel Orthosilicate**, Ni₃SiO₉, has been prepared by prolonged heating to redness of amorphous silica intimately mixed with nickel oxide and chloride. It yields greenish yellow crystals of density 4.85.

An acid silicate, of composition NiO.5SiO₂.4H₂O, is described as resulting by the interaction of sodium silicate and a nickel salt in aqueous solution.

**Nickel Fluosilicate**, NiSiF₆.6H₂O, and **Arsenosilicide**, Ni₅As, have been described.

**Nickel Stannate**, NiO.SnO₁₇.5H₂O; **Fluostannate**, NiSnF₆.6H₂O; and **Chlorostannate**, NiSnCl₆.6H₂O are also known.

**Nickel and Boron**

Several borides of nickel are known to science.

**Nickel Monoboride**, NiB, is obtained as brilliant prisms of density 7.39, by heating nickel and boron in an electric furnace. It is decomposed upon fusion with alkali.

By heating mixtures of nickel and boron in a current of hydrogen at 1100–1200° C., du Jassonneix has prepared two borides of nickel,

namely, the Sub-boride, \( \text{Ni}_2\text{B} \), and the Diboride, \( \text{NiB}_2 \). The former yields small, slender, yellow acicular crystals of density 8.0 at 20°C. These are slightly oxidised by moist air, but are violently attacked by nitric acid. Indications have been obtained of the formation of a sesquiboride, \( \text{Ni}_2\text{B}_3 \).

**Nickel Borates.**—Several borates of nickel have been described. The tetraborate, \( \text{NiO} \cdot 4\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O} \), is obtained \(^2\) by slow evaporation of a solution of nickel carbonate in boric acid. The precipitate first formed becomes crystalline gradually, yielding small brilliant and clear green crystals; soluble in cold water, but becoming turbid at 40°C.

On fusing nickel chloride or carbonate with molecular proportions of potassium hydrogen fluoride and boric oxide, green prisms of \( 8\text{NiO} \cdot \text{B}_2\text{O}_3 \) are obtained.\(^3\) They are not attacked by hot water, but dissolve in acids.

A diborate, \( \text{NiO} \cdot 2\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \), has also been obtained.\(^2\)

Chloro,\(^4\) bromo,\(^4\) and iodo\(^5\) borates are known.

Nickel borate has been recommended as a catalyst in the hydrogenation of unsaturated oils (see p. 95), but its action is attributable to nickel liberated by the hydrogen,\(^6\) and not to any inherent catalytic power of the borate itself.\(^7\) It offers no advantage over nickel oxide.\(^8\)

**DETECTION AND ESTIMATION OF NICKEL**

**Detection.**—*Dry Tests.*—Nickel salts are usually green in colour when hydrated, but yellow when anhydrous. They impart a reddish brown colour to the borax bead when heated in the oxidising flame of the blowpipe, but dark and opaque in the reducing flame.

**Wet Tests.**—For the detection of minute quantities in an alloy, Fortini recommends the application of a drop of the following solution upon the slightly oxidised surface of the metal, namely:

- 0.5 gram dimethyl glyoxime.
- 5.0 c.c. 98 per cent. alcohol.
- 5.0 c.c. conc. ammonium hydroxide.

Traces of nickel oxide yield red specks in a few seconds, before any copper which may be present has had time to mask the reaction by yielding a blue colour.\(^9\)

In qualitative analysis by wet methods nickel is precipitated from its solution as black, hydrated oxide, as explained under Cobalt (see p. 75).

**Estimation.**—*Gravimetric Methods.*—A convenient method consists in decomposing a solution of nickel salt with sodium hypobromite as explained on p. 118, and either reducing the oxide in a current of hydrogen and weighing as metallic nickel, or by ignition in air and

---

weighing as the monoxide, NiO. Nickel may also be precipitated from its ammoniacal or acetic acid solution by addition of an alcoholic solution of \( \alpha \)-dimethyl glyoxime. The voluminous scarlet precipitate is filtered through a Gooch crucible packed with asbestos and dried at 110° to 120° C. The nickel is either weighed as \( \text{C}_8\text{H}_{14}\text{Ni}_4\text{O}_4\text{Ni} \), which contains 20.88 per cent. of metal,\(^1\) or ignited and weighed as oxide.\(^2\) Even more sensitive is \( \alpha \)-diphenyl glyoxime (\( \alpha \)-benzil dioxime), which gives with nickel compounds a bulky red precipitate, insoluble in water, alcohol, acetone, ammonia, and 10 per cent. acetic acid. It becomes reddish yellow on boiling. One part of nickel per 5,000,000 of water may be detected by this reagent.\(^3\) The estimation of nickel is conducted in a precisely similar manner to that with the dimethyl derivative, the precipitate being dried at 110° to 112° C., and containing 10.98 per cent. of nickel. The formula of the precipitate is \( \text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{Ni} \).

**Volumetric Methods.**—Nickel may be conveniently estimated volumetrically in the absence of cobalt, copper, silver, gold, and the platinum metals by means of potassium cyanide.\(^4\) The solution containing the nickel is, if acid, neutralised with ammonia and some ammonium sulphate is added to render the indicator more sensitive. A little ammonia is now added, and a few drops of potassium iodide and silver nitrate. The solution becomes turbid in consequence of the precipitation of silver iodide. The liquid is now titrated with potassium cyanide solution until the turbidity just disappears. The reaction consists in converting the nickel salt into the double cyanide, \( \text{Ni(CN)}_2.2\text{KCN} \), after which any excess of potassium cyanide attacks the silver iodide, yielding the soluble double cyanide, \( \text{AgCN.KCN} \). The disappearance of the turbidity therefore indicates the complete conversion of the nickel salt.\(^5\) A slight correction is necessary for the silver introduced.

**Electrolytic Methods** have been employed.\(^6\)

---

1. For details of analysing an ore containing cobalt and nickel see p. 76.
CHAPTER IV
RUTHENIUM AND ITS COMPOUNDS

RUTHENIUM

Symbol, Ru. Atomic weight, 101.7 (O = 16)

Occurrence and History.—The name ruthenium is due to Osann, who obtained what he believed to be the oxide of a new metal from the Ural platinum ores. This oxide was subsequently investigated by Claus, who found that, although it contained a high proportion of the oxides of silicon, zirconium, titanium, and iron, it nevertheless possessed a small quantity of a new oxide for which he retained the name used by Osann.

Ruthenium occurs alloyed with platinum ores and osmiridium, as indicated in the tables of analyses (pp. 208, 258). Combined with sulphur it is found as the rare mineral laurite, Ru₂S₃, which occurs in platinum washings in Borneo and Oregon. That ruthenium is present in celestial bodies is evidenced by the fact that it was detected in the Perryville siderite discovered in 1906 (see this volume, Part II).

Preparation.—Ruthenium may be conveniently prepared from osmiridium, which is an alloy of osmium and iridium containing small proportions of rhodium and ruthenium, the last named amounting in some cases to 6 per cent. (see analyses, p. 208).

The alloy is heated to a white heat with four or five times its weight of zinc in a carbon crucible until the vapour of zinc ceases to be evolved. The friable mass left is crushed and heated with a mixture of barium dioxide and nitrate to about 900°C. in an earthenware crucible. On cooling, the powdered mass is treated with dilute hydrochloric acid, care being taken to keep the temperature down by immersion of the containing vessel in cold water. A fume-cupboard with a powerful draught is desirable in view of the presence of poisonous osmic tetroxide in the evolved vapours.

When the reaction has subsided, nitric and sulphuric acids are added, whereby barium sulphate is precipitated. The clear solution is decanted and distilled until one-quarter of its volume has been collected as distillate. This latter liquor is rich in osmium, and may be worked for that metal (see p. 208). The residue is evaporated to small bulk. Ammonium chloride and a small quantity of nitric acid are added, and the mixture evaporated to dryness on the water-bath. A violet-black crystalline solid is obtained which is washed with water half saturated with ammonium chloride until the filtrate is colourless. The insoluble residue consists of fairly pure ammonium chlor-iridate containing ruthenium, from which the spongy metals are obtained by ignition.

1 Osann, Pogg. Annalen, 1828, 14, 329; 1845, 64, 197.
2 Claus, Annalen, 1845, 56, 287; 1846, 59, 234; Pogg. Annalen, 1845, 64, 192; 65, 200.
3 Wöhler, Annalen, 1866, 139, 116.
It now remains to separate out the ruthenium. This is accomplished by fusing with potassium hydroxide and nitrate, best in a silver crucible, and subsequently dissolving in water. The solution obtained has an orange-yellow colour in consequence of the presence of potassium ruthenate. This colour is removed by the addition of nitric acid, ruthenium oxide separating out. Ignition in a graphite crucible with a little chalk yields the free ruthenium, the chalk combining with any silicon, chromium, and osmium that may have been present.

Further purification may be effected by one or more additional fusions of the metal with potassium hydroxide and nitrate.

As obtained in this way the metal is not pure, but contains small quantities of alloyed elements such as osmium and iridium.

Chemically Pure Ruthenium may be obtained by the foregoing by maintaining it, in the form of a fine powder, at a dull red heat in a current of oxygen for about three hours, whereby the osmium content is quantitatively oxidised to the volatile tetroxide, OsO₄, which is driven off. The ruthenium also undergoes partial oxidation, and is now reduced in a current of pure hydrogen. It is then fused, preferably in a silver vessel, with excess of potassium hydroxide and nitrate, cooled, and extracted with water. The orange-coloured solution, containing potassium ruthenate, is gently distilled in a current of chlorine whereby volatile ruthenium tetroxide is produced, and is absorbed in aqueous potassium hydroxide. Since all the osmium has been removed, the distillate of ruthenium tetroxide is exceedingly pure, for the residue contains no other metal yielding a volatile product under these conditions. Upon addition of absolute alcohol to the potash solution a black precipitate is obtained containing ruthenium in a more or less completely reduced condition, reduction being finally completed by ignition in a current of pure hydrogen.

Crystalline Ruthenium may be obtained by fusing the metal with excess of tin in a carbon crucible, whereby the compound, RuSn₃, is formed. Treatment with boiling hydrochloric acid removes the excess of tin, and the unattacked residue of RuSn₃ is ignited in a current of hydrogen chloride. The combined tin is thereby removed as a volatile chloride, leaving behind crystalline ruthenium. Cubic and fernlike crystals are obtained by ignition of the finely divided metal at a high temperature with borax and pyrites.

Physical Properties.—In the compact form ruthenium is a hard, brittle metal, resembling platinum in appearance and lustre. When powdered it has a dull grey colour. Its density varies greatly according to its physical condition, as is usually the case. After fusion, the value 12.068 has been obtained. Like palladium, ruthenium readily occludes gases, and when used as cathode in the electrolysis of acidulated water it absorbs the hydrogen, retaining it for a long time.

1 Gutbier and Trenkner, Zeitsch. anorg. Chem., 1905, 45, 186.
2 It is important to ensure complete solution of the ruthenium tetroxide, otherwise the addition of alcohol causes reactions to take place with explosive violence (Howe, J. Amer. Chem. Soc., 1901, 23, 775; Gutbier and Trenkner, loc. cit.).
4 Deville and Debray, Compt. rend., 1879, 89, 590.
5 Joly, Compt. rend., 1893, 116, 430. Other values are 8.6 for the porous metal (Clais, Annalen, 1845, 56, 257); 12.062 for the metal obtained by reduction of the dioxide (Violle).
6 Caillletet and Collardeau, Compt. rend., 1894, 119, 830.
The specific heat of the powdered metal between 0° and 100° C. is 0.0611, and 0.0595 for the compact metal. Ruthenium may be fused in the oxyhydrogen flame and distilled in the electric furnace, so that its melting- and boiling-points may be taken as of the order of 1900° C. and 2520° C. respectively.

The most intense lines in the spectrum of ruthenium are as follow:

Arc: 3417-50, 3428-50, 3436-87, 3499-09, 3593-18, 3596-31, 4080-78.

Finely divided ruthenium acts as a catalyst, inducing, for example, the oxidation of alcohol to aldehyde and acetic acid in the presence of air.

**Colloidal Ruthenium.**—Ruthenium may be obtained in the colloidal condition by reduction of its salts in aqueous solution by hydrazine hydrate in the presence of gum acacia. Other reducing agents may be employed for the same purpose, such as acrolein.

**Ruthenium Sponge** results on ignition of ammonium chlor-ruthenate. It readily dissolves in a solution of hydrogen chloride saturated with chlorine yielding halogen derivatives. Hydrobromic acid saturated with bromine likewise effects the solution of ruthenium sponge.

**Explosive Ruthenium** is obtained by dissolving an alloy of the metal with excess of zinc in hydrochloric acid. The zinc passes into solution, leaving metallic ruthenium as a finely divided, explosive residue. Unlike rhodium and iridium, ruthenium is explosive even when prepared in the entire absence of air. It seems hardly possible, therefore, that the same explanation for the explosiveness can apply as for the first two metals (see pp. 156, 239). Perhaps Bunsen's original explanation is the correct one, namely, that an unstable modification or allotrope is first formed, and that this is converted into the stable variety with considerable heat evolution.

**Chemical Properties.**—When heated in air ruthenium becomes covered with a brown film of oxide and, on cooling, "spits" in a similar manner to iridium and silver. Heated in oxygen, particularly when in a fine state of division, it yields the dioxide, RuO₂, and at 600° C. some tetroxide, RuO₄, begins to be formed. Previous ignition in hydrogen to a high temperature reduces the velocity of oxidation of ruthenium. Mineral acids have no action upon ruthenium, and aqua regia only slowly dissolves it.

When heated in fluorine a volatile fluoride is formed, and in chlorine a chloride is obtained, possibly the dichloride, RuCl₂. Ignition with potassium chloride in a current of chlorine yields potassium chlor-ruthenate, which is soluble in water.

---

Alkali hypochlorites effect the solution of ruthenium when fused, but the best mixture to employ consists of potassium hydroxide and nitrate, a green mass of potassium ruthenate, \( K_2RuO_4 \), being formed. This dissolves in water to an orange-coloured solution, which leaves a black stain upon the skin.

Fusion with potassium hydrogen sulphate is without effect upon ruthenium, although in like circumstances rhodium, palladium, and iridium are attacked.

**Atomic Weight.**—Approximate Atomic Weight.—That the atomic weight of ruthenium is approximately 100 and not a multiple or sub-multiple of this amount is evident from various considerations, namely:

1. Its specific heat is 0.0611. Assuming a mean atomic heat of 6.4, the atomic weight of ruthenium, according to Dulong and Petit's Law, is approximately 105.

2. The most appropriate position for ruthenium in the Periodic Table is as the first member of the second series of horizontal triads. Hence its atomic weight should lie between that of molybdenum (96) and rhodium (102.9), but nearer in point of magnitude to the last named since an element should be in Group VII between it and molybdenum, but has yet to be discovered.

3. The alkali chlor-ruthenates are isomorphous with the chlor-platinates, and therefore, by the application of Mitscherlich's Law, they must be assumed to contain, like the platinum derivatives, one atom of ruthenium, their generic formula being \( M_2RuCl_6 \). Similarly, ruthenium dioxide is isomorphous with cassiterite, \( SnO_2 \), and with rutile, \( TiO_2 \), from which it may be concluded that its formula is \( RuO_2 \). Analyses of these compounds indicate that the atomic weight of ruthenium is 101.7.

**Exact Atomic Weight.**—For many years the accepted value for the atomic weight of ruthenium was 108, a figure derived from the work of Claus.1 This chemist decomposed potassium chlor-ruthenate, \( K_2RuCl_5 \), by heating it in a stream of hydrogen, noted the loss in weight, and separated and determined the amounts of ruthenium and potassium chloride in the residue. From his values for the percentages of ruthenium, potassium chloride, and chlorine expelled, the corresponding atomic weights deduced for ruthenium are 108.2, 107.4, and 97.1 respectively. These results are obviously of no present value.

In 1889, Joly2 determined the percentage of ruthenium in three pure ruthenium compounds, viz. (i) ruthenium dioxide, \( RuO_2 \), (ii) ruthenium nitrosochloride, \( Ru(NO)Cl_3 \cdot H_2O \), and (iii) ammonium nitrosochlor-ruthenate, \( (NH_4)_2Ru(NO)Cl_5 \). In each case reduction to the metal was brought about by heating the compound in a stream of hydrogen. The mean results were as follow:

\[
\begin{align*}
\text{Ru} &: RuO_2 : 76.060 : 100.000 \\
\text{2 expts.} & \quad \text{Ru} : Ru(NO)Cl_3 \cdot H_2O : 39.720 : 100.000 \\
\text{2 expts.} & \quad \text{Ru} : (NH_4)_2Ru(NO)Cl_5 : 59.465 : 100.000 \\
\end{align*}
\]

whence \( Ru = 101.668 \)

\[
\begin{align*}
\text{Ru} &: RuO_2 : 76.060 : 100.000 \\
\text{2 expts.} & \quad \text{Ru} : Ru(NO)Cl_3 \cdot H_2O : 39.720 : 100.000 \\
\text{2 expts.} & \quad \text{Ru} : (NH_4)_2Ru(NO)Cl_5 : 59.465 : 100.000 \\
\end{align*}
\]

whence \( Ru = 101.734 \)

whence \( Ru = 101.615 \)

In 1912, Vogt3 analysed ruthenium dioxide by reducing it to the metal in a stream of hydrogen, obtaining as a mean of six experiments, the following result:

\[
\begin{align*}
\text{Ru} &: RuO_2 : 76.053 : 100.000 \\
\end{align*}
\]

whence \( Ru = 101.63 \)

3 The antecedent data are as follow: \( O = 16.000 \), \( N = 14.008 \), \( Cl = 35.457 \), \( H = 1.00762 \).
The International Committee for 1918 on Atomic Weights accepts the value $\text{Ru} = 101.7$. Further determinations of this constant are clearly desirable.

**Alloys.**—Ruthenium forms a beautiful crystalline alloy with tin,\(^1\) which is cubic in structure. It is readily formed by heating to redness in a carbon crucible one part of ruthenium with 10–15 parts of tin. On cooling, the excess of tin is dissolved out by treatment with hydrochloric acid, the residue having the composition represented by the formula $\text{RuSn}_3$.

An alloy with zinc was also prepared by Deville and Debray, which yielded hexagonal prisms, and was combustible in air with feeble deflagration. Its composition was not determined. Ruthenium dissolves in lead, but yields no compound with it. On treatment with acid the lead dissolves, leaving the ruthenium as a crystalline residue.\(^2\)

**RUTHENIUM AND THE HALOGENS**

Ruthenium combines with all four of the halogen elements.

**Ruthenium Fluoride**, $\text{RuF}_3$, results as a volatile substance when the finely divided metal is heated to redness in fluorine. It occurs under these conditions as a dense, coloured vapour.\(^3\)

**Ruthenium Dichloride**, $\text{RuCl}_3$, was stated by Claus\(^4\) to result when chlorine is passed over heated ruthenium. Repetition of the experiment by Gutbier and Trenkner\(^5\) in 1906 led to no definite result, varying amounts of chlorine being absorbed, but always considerably less than theory requires for the dichloride. The experiments were by no means exhaustive, and do not justify the assumption that the dichloride cannot be prepared in this way. As Gutbier points out, it is quite possible that a reversible reaction takes place between the ruthenium and chlorine, thus:

$$\text{Ru} + \text{Cl}_2 \rightleftharpoons \text{RuCl}_2.$$  

In view of the catalytic activity of the metals discussed in this volume the subject is worthy of more careful investigation.

Some forty years before the discovery of ruthenium by Claus, it had been observed by Vauquelin that an azure blue colour is obtained by the action of zinc on certain solutions. This was attributed to the presence of osmium, but is now known to be a characteristic reaction for trivalent ruthenium. A similar colour is obtained by the action of hydrogen sulphide upon ruthenium trichloride, and was attributed by Claus and Joly\(^6\) to reduction to the dichloride. This view is supported by Howe,\(^7\) who, however, has not succeeded in isolating the salt, but has obtained a derivative to which he gives the formula:

$$3\text{CsCl} \cdot 2\text{RuCl}_2 \cdot 2\text{H}_2\text{O}.$$  

This salt is readily formed by the reduction of ruthenium trichloride in an electrolytic cell, and immediately adding a concentrated solution

---

of caesium chloride to the blue liquid. A fine precipitate results, varying
in colour from a dark greenish blue to olive green, and which oxidises
with great rapidity, rendering analysis difficult.

Ruthenium Trichloride, RuCl₃, is conveniently prepared by warming
the tetroxide with concentrated hydrochloric acid on the water-bath.
Chlorine is vigorously evolved, the reaction proceeding according to
the equation:

\[
2\text{RuO}_4 + 16\text{HCl} = 2\text{RuCl}_3 + 5\text{Cl}_2 + 3\text{H}_2\text{O}.
\]

The reaction, if slow to begin, may be started by the addition of a
few drops of alcohol. Gutbier prepared the salt by treating the tetroxide,
RuO₄, with 20 per cent. hydrogen chloride solution and allowing it to
stand under reduced pressure for two hours. The solution thus obtained
was freed from chlorine and unaltered oxide and concentrated to a
syrup by passage of air over the warmed liquid. Exposure over concen-
trated sulphuric acid in a vacuum desiccator left the crystalline salt
as a black mass.¹ The trichloride is also formed by dissolving the
tetroxide in chlorine water. On evaporation a lustrous, somewhat
hygroscopic mass of trichloride remains behind which is readily soluble
in water and in alcohol, yielding an orange-yellow solution. The
aqueous solution is very sensitive to rise in temperature, and decom-
poses even at 50° C. into a black hydrated oxide or oxychloride and
free hydrochloric acid. The colour of the precipitate is so intense that
one part of the metal distinctly darkens 100,000 parts of water.

Ruthenium trichloride begins to be reduced by hydrogen ² at 190° C.,
it readily absorbs dry ammonia gas,³ yielding a black-violet addition
compound, 2RuCl₃.7NH₃, which dissolves in water to a bright red
solution. Heat is set free during the absorption of ammonia, but if
the temperature is maintained at 0° C. the reaction is complete.

Chlor-ruthenites or Ruthenochlorides, M₂RuCl₅

Double salts of ruthenium trichloride and the chlorides of the
alkali metals have been prepared and are known as chlor-ruthenites
or ruthenochlorides, their general formula being RuCl₃.2MCl or M₂RuCl₅.
The first of these to be discovered was:

Potassium Chlor-ruthenite, K₂RuCl₅.—This salt may be prepared
by the reduction of ruthenium nitrosotritylhydroxide, Ru(NO)(OH)₂, in
alkaline solution by boiling with formaldehyde, dissolving in hydro-
chloric acid, and separating out the salt by addition of potassium
chloride.⁴ Obtained in this way the crystals are brown in colour.

The salt may be prepared in an impure form by dissolving ruthenium
in fused potassium hydroxide, adding small quantities of potassium
nitrate the while, until all the ruthenium has passed into solution. On
cooling the green mass becomes orange, and treatment with concen-
trated hydrochloric leaves a residue of potassium chlor-ruthenite.⁵

A convenient method of preparing a fairly pure specimen of potas-
sium chlor-ruthenite consists in adding freshly distilled ruthenium
tetroxide to concentrated hydrochloric acid and digesting on the water-
bath until evolution of chlorine ceases. This requires about two days.

¹ Gutbier, Ztschr. angew. Chem., 1909, 22, 487.
³ Joly, Compt. rend., 1892, 115, 129.
⁵ Antony and Lucchesi, Gazzetta, 1899, 29, ii, 82.
To the resulting strongly acid solution of ruthenium trichloride, potassium chloride is added in small quantities at a time, whereby a precipitate of crystals of potassium chlor-ruthenate is obtained. These are washed free from acid with alcohol, and dried by exposure over concentrated sulphuric acid.\(^1\)

Potassium chlor-ruthenate rapidly hydrolyses in aqueous solution, the liquid, originally red, gradually becoming black. The velocity of the hydrolysis admits of determination by electric conductivity measurements in consequence of the hydrochloric acid set free.\(^2\)

The equilibrium of the hydrolysed solution is not altered by dilution, by addition of acid, or by change of temperature. It thus appears that the reaction is irreversible, and that the final state does not represent a true equilibrium.

The reaction appears to take place according to the equation:

\[
K_2RuCl_5 + 2H_2O = 2KCl + 2HCl + Ru(OH)_2Cl.
\]

Addition of alkali hydroxide to the hydrolysed solution yields an immediate precipitate of hydrated ruthenium sesquioxide, \(Ru_2O_3\cdot3H_2O\).\(^3\)

Of particular interest is Cæsium Chlor-ruthenate, \(Cs_2RuCl_5\cdotH_2O\), which Howe\(^4\) obtained by the action of hydrochloric acid on ruthenium tetroxide and subsequent addition of cæsium chloride to the solution. The salt is precipitated as a dark brown powder, fairly soluble in water and hydrochloric acid, exhibiting the chemical reactions of a trivalent ruthenium salt. Howe also describes an isomeride of this salt, which he termed, in accordance with Werner's nomenclature, Cæsium Aquochlor-ruthenate (vide infra).

Rubidium Chlor-ruthenate is also known.\(^4\)

Ruthenium Tetrachloride, \(RuCl_4\), probably exists in solution when the hydrated dioxide, obtained by the action of caustic alkali on the sulphate, is dissolved in hydrochloric acid. It yields a yellow solution from which the tetrachloride cannot be isolated in a pure condition,\(^5\) although double salts with the alkali metals have been obtained. These are known as:

*Chlor-rutenates or Ruthenichlorides, \(M_2RuCl_6\).

Potassium Chlor-ruthenate, \(K_2RuCl_6\), may be prepared by adding hydrochloric acid to potassium ruthenate.\(^6\) The method adopted by Antony and Lucchesi\(^7\) consists in heating ruthenium with six times its weight of fused potassium hydroxide in a silver dish. Potassium chlorate is added little by little, and the whole stirred until all the ruthenium has dissolved. The heating is continued until evolution of gas ceases, indicating complete decomposition of the chlorate. On cooling, the orange-red-coloured melt is dissolved in cold water, and dilute hydrochloric acid added until the whole is slightly acid. Concentration is effected over quicklime until the salt crystallises out in reddish brown crystals. Potassium chlor-ruthenate may also be

\(^3\) Lind and Bliss, *loc. cit.*
\(^5\) Howe, *ibid.*, 1904, 26, 543; see also Miolati and Tagiuri, *Gazzetta*, 1900, 30, [ii], 511.
\(^7\) Antony and Lucchesi, *Gazzetta*, 1899, 29, [ii], 82.
obtained by the action of chlorine\(^1\) on a concentrated, acidulated solution of potassium aquo-chlor-ruthenate, \(K_2\text{Ru(OH}_2\text{)}\text{Cl}_5\). It then crystallises in minute black octahedra possessed of a greenish sheen, and which are easily soluble in and rapidly decomposed by water. In hydrochloric acid a pure yellow colour is obtained if the solution is dilute, the concentrated solution being deep yellowish red.

Ammonium, rubidium, and caesium chlor-ruthenates have also been prepared.\(^2\)

Potassium Aquo-chlor-ruthenate, \(K_2\text{Ru(OH}_2\text{)}\text{Cl}_5\), results\(^1\) on boiling a slightly acidified solution of potassium chlor-ruthenate, \(K_2\text{RuCl}_5\), with alcohol; as also by heating the hydrated sesquioxide with hydrochloric acid and alcohol.

Upon evaporation the salt crystallises in orthorhombic octahedra, which are soluble in water. The solution yields with alkalis a dirty white precipitate which soon becomes black, thereby differing from solutions of the trichloride, which give an immediate black precipitate under such conditions.

Potassium Nitroso-chlor-ruthenate, \(K_2\text{Ru(NO)}\text{Cl}_5\), is known (see p. 150).

Cesium Aquo-chlor-ruthenate, \(Cs_2\text{Ru(OH}_2\text{)}\text{Cl}_5\), is an interesting salt inasmuch as it is isomeric with the first chlor-ruthenate to be discovered, namely, \(Cs_2\text{RuCl}_5\cdot\text{H}_2\text{O (vide supra)}\). It is obtained\(^3\) as a buff precipitate on adding alcohol to the blue filtrate from electrically reduced solutions of ruthenium trichloride and caesium chloride. On crystallisation, rose-coloured prisms are obtained. These are soluble in water, and may be recrystallised unchanged from aqueous hydrochloric acid.

Oxychlorides.—When ruthenium tetroxide is covered with water, to which caesium chloride acidulated with hydrochloric acid is subsequently added, caesium oxychlor-ruthenate,\(^8\) \(Cs_2\text{RuO}_2\text{Cl}_4\) or \(2\text{CsCl.RuOCl}_2\), is formed. On crystallisation dark purple isometric octahedra, cubes, and rhombic dodecahedra separate out. These are soluble in cold hydrochloric acid, from which they may be recrystallised unchanged.

The reaction may be represented as follows:

\[
\text{RuO}_4 + 4\text{HCl} + 2\text{CsCl} = \text{Cs}_2\text{RuO}_2\text{Cl}_4 + 2\text{H}_2\text{O} + \text{Cl}_2.
\]

A characteristic reaction for these crystals is their behaviour towards water, which instantly decomposes them, the water becoming black.

On boiling with concentrated hydrochloric acid chlorine is disengaged, caesium chlor-ruthenate remaining behind. Thus:

\[
\text{Cs}_2\text{RuO}_2\text{Cl}_4 + 4\text{HCl} = \text{Cs}_2\text{RuCl}_6 + 2\text{H}_2\text{O} + \text{Cl}_2.
\]

Ruthenium Tribromide, \(\text{RuBr}_3\), is most readily obtained by evaporation of an aqueous solution of the tetroxide with concentrated hydrobromic acid\(^4\):

\[
2\text{RuO}_4 + 16\text{HBr} = 2\text{RuBr}_3 + 5\text{Br}_2 + 8\text{H}_2\text{O}.
\]

The salt is dark brown in colour dissolving in water to a bright red solution, which decomposes slowly on keeping, but rapidly on warming,

\(^1\) Howe, J. Amer. Chem. Soc., 1904, 26, 543; see also Mioleti and Tagiri, Gazzetta, 1900, 30, [ii], 511.

\(^2\) See Howe, loc. cit. Substituted ammonium chlor-ruthenates, such as, for example, the methyl derivative, \((\text{CH}_3\cdot\text{NH}_2)_2\text{RuCl}_4\), etc., have been prepared by Gutbier and Zwicker, Ber., 1907, 40, 690.

\(^3\) Howe, J. Amer. Chem. Soc., 1901, 23, 775.

\(^4\) Gutbier and Trenkner, Zeitsch. anorg. Chem., 1905, 45, 166.
yielding a black precipitate. With sulphuretted hydrogen the solution yields ruthenium sulphide.

When heated the solid bromide evolves bromine. It absorbs dry ammonia gas, yielding an addition compound of composition\(^1\) \(2\text{RuBr}_3\cdot 7\text{NH}_3\).

With bromides of the alkali metals double salts known as bromruthenites are formed. Of these the potassium salt is most important.

**Potassium Bromruthenate**, \(\text{K}_2\text{RuBr}_6\), is formed when potassium bromide is added to a solution of ruthenium tetroxide in hydrobromic acid. Upon concentration over sulphuric acid small brown crystals are obtained, readily soluble, with decomposition, in water.\(^2\)

The corresponding ammonium, rubidium, and cesium derivatives have been prepared.

Although the tetrabromide of ruthenium has not been isolated, double salts known as bromruthenates, have been prepared.

**Potassium Bromruthenate**, \(\text{K}_2\text{RuBr}_6\), is obtained\(^3\) by passing a current of bromine vapour through a concentrated solution of potassium aquobromruthenate cooled to 0°C. A precipitate of minute crystals is obtained, octahedral in shape, and very soluble in water.

**Potassium Aquobromruthenate**, \(\text{K}_2\text{Ru(OH)}_2\text{Br}_5\), may be prepared\(^3\) by boiling potassium bromruthenate with alcohol and hydrobromic acid. On standing, minute brown crystals, having the above composition, separate out.

The corresponding rubidium and cesium salts are also known.\(^3\)

**Ruthenium Tri-iodide**, \(\text{RuI}_3\), was prepared by Claus\(^4\) by double decomposition of potassium iodide and ruthenium trichloride in aqueous solution.\(^5\) The salt separates out as a black amorphous precipitate which, on heating, evolves the whole of its iodine content. It absorbs ammonia, yielding \(2\text{RuI}_3\cdot 7\text{NH}_3\), but does not appear to yield double salts with alkali iodides.\(^5\)

## RUTHENIUM AND OXYGEN

Ruthenium combines with oxygen in several different proportions. A monoxide, \(\text{RuO}\), was stated by Claus\(^6\) to result when the dichloride, \(\text{RuCl}_2\), is heated with slightly more than one equivalent of sodium carbonate in a current of carbon dioxide. This result was apparently accepted until 1905, in which year Gutbier and Trenkner,\(^7\) as has already been mentioned, threw doubt on the supposed existence of ruthenium dichloride. This raised the question as to whether or not the monoxide could exist. Experiments carried out by Gutbier and Ransohoff with a chloride of ruthenium and sodium carbonate after the manner described by Claus gave very uncertain results, from which it may be concluded that ruthenium monoxide has not as yet been prepared, and is possibly incapable of a separate existence. The

---

\(^1\) Gutbier and Trenkner, *Zeitsch. anorg. Chem.*, 1905, 45, 166.


\(^3\) Howe, loc. cit. Substituted ammonium bromruthenates are described by Gutbier and Zwicker, *Ber.*, 1907, 40, 690.


\(^6\) Claus, *Annalen*, 1846, 59, 234.

evidence, however, is by no means exhaustive, and further work on the subject might lead to interesting results.

In the following table are given the various oxides and hydrated oxides of ruthenium which were assumed by Claus and by Debray and Joly. The final column mentions those whose existence has now been fairly definitely established, largely through the researches of Gutbier

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RuO</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ru₂O₃</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ru(OH)₃</td>
<td>—</td>
<td>Ru₂O₃</td>
</tr>
<tr>
<td>RuO₂</td>
<td>RuO₂</td>
<td>Ru(OH)₃</td>
</tr>
<tr>
<td>Ru(OH)₄·3H₂O</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>—</td>
<td>Ru₂O₉</td>
<td>—</td>
</tr>
<tr>
<td>—</td>
<td>Ru₂O₅</td>
<td>—</td>
</tr>
<tr>
<td>RuO₃</td>
<td>Ru₂O₅·2H₂O</td>
<td>Ru₂O₃</td>
</tr>
<tr>
<td>—</td>
<td>Ru₂O₇</td>
<td>Ru₂O₅</td>
</tr>
<tr>
<td>—</td>
<td>RuO₄</td>
<td>RuO₄</td>
</tr>
</tbody>
</table>

**Ruthenium Sesquioxide**, Ru₂O₃.—When strongly heated in air ruthenium yields a bluish black oxide which is not reduced at white heat. Claus believed that the sesquioxide, Ru₂O₃, could be produced in this way, but Gutbier and Ransohoff have adduced evidence in favour of the assumption that the product is not a well-defined oxide, but an intimate mixture of ruthenium and its dioxide, RuO₂. No other method tried by the last-named authors yielded the sesquioxide in the anhydrous condition, although decomposition of the corresponding hydroxide, Ru₄(OH)₆ (see below), by ignition in a current of carbon dioxide gave indications that the oxide is capable of existence.

**Hydrated Ruthenium Sesquioxide**, Ru₂O₅·3H₂O or Ru₄(OH)₆, was prepared by Gutbier and Ransohoff by addition of sodium hydroxide to an aqueous solution of ruthenium sesquichloride, Ru₂Cl₆. A blackish brown amorphous precipitate was obtained which was dried in a vacuum desiccator over sulphuric acid. Analysis yielded figures agreeing fairly well with the formula given above, but it was not found possible to remove the last traces of alkali, even by washing with very dilute hydrochloric acid. Ignition in a current of hydrogen yields the pure metal.

Ruthenium hydroxide is obtained in colloidal form by reducing an aqueous solution of potassium chlor-ruthenite, K₂RuCl₅, by hydrazine sulphate in the presence of gum acacia, which serves as a protective colloid, preventing the coagulation of the hydroxide.  

1 This table is taken from Gutbier, Zeitsch. anorg. Chem., 1916, 95, 178.
2 These oxides do not appear to be capable of a separate existence, although their derivatives are well known.
3 Claus, Annalen, 1845, 56, 257; Pogg. Annalen, 1845, 64, 192; 65, 200.
4 Claus, Annalen, 1846, 59, 234.
Ruthenium Dioxide, RuO₂, is obtained as a sublimate by heating ruthenium in a current of oxygen. The metal may thus be extracted, along with osmium in the form of its more volatile tetroxide, OsO₄, from osmiridium by heating the last named in oxygen (or air) to about 1080° C. If the mixed vapours are passed through a heated porcelain tube ruthenium dioxide condenses first.

If the ruthenium is finely powdered, the oxidation begins at 600° C. and increases rapidly with the temperature, being 4000 times as rapid at 1200° C. as at 700° C. Crystals of the dioxide may be detected in the sublimate. Previous ignition in hydrogen to a high temperature reduces the velocity of oxidation of the metal.

The dioxide may also be obtained by heating the sulphate or disulphide in the presence of air. It crystallises in the form of hard, tetragonal pyramids, of density 7.2, and isomorphous with cassiterite and rutile. The crystals exhibit a green iridescent metallic lustre. They are not acted upon by acids, but yield potassium ruthenate when fused with potassium hydroxide.

The dioxide undergoes partial dissociation at temperatures above 1000° C., and when heated in vacuo the oxygen tension amounts to 15 to 17 mm. at 1000° C., and a little metallic ruthenium remains behind on cooling beneath the layer of dioxide.

Ruthenium dioxide is obtained in the hydrated condition, RuO₂.2H₂O, as a dark red precipitate by heating the sulphate with potassium hydroxide solution. On heating to 300° C. it loses water, and at higher temperatures deflagrates with incandescence. It dissolves in acids and alkalies to yellow-coloured solutions. Claus gave the formula Ru(OH)₄.2H₂O to the precipitate, but Gutbier and Ransohoff show that the composition is variable.

Ruthenites.—Ruthenium dioxide unites with metallic oxides to yield ruthenites of general formula M₂RuO₃. The best-known salt is barium ruthenate, BaRuO₃, which is obtained by heating barium ruthenate to 440° C. in vacuo, when oxygen is evolved and a bluish black residue of ruthenite remains, which is insoluble in water. Treatment with hydrochloric acid converts it into the trichloride.

Ruthenium Tetroxide, Ruthenium Peroxide, RuO₄, results in small quantity when ruthenium is heated to about 1000° C. in a current of oxygen. A more convenient method of preparing it is that first adopted by Claus, and consists in passing chlorine through a solution of alkali ruthenate and warming to 80° to 90° C. The tetroxide distils over and, on cooling, yields a golden yellow mass. It may be purified by repeated shaking with warm water to remove all traces of chlorine, separating as completely as possible from water, and finally subliming several times in vacuo, when it yields beautiful crystals melting at 25-5° C. to an orange liquid, and decomposing at 106° to 107° C., yielding the crystalline dioxide. Its vapour density at 100° C. as determined

1 Gutbier and Ransohoff, Zeitsch. anorg. Chem., 1905, 146.
4 Debray and Joly, Compt. rend., 1888, 106, 100.
6 Joly, Compt. rend., 1891, 113, 694.
RUTHERNIUM AND ITS COMPOUNDS

by Dumas' method \(^1\) corresponds to a molecular weight of 166.7. Theoretically the formula RuO\(_4\) requires the value 165.7. The vapour vigorously attacks cork and rubber.

Ruthenium tetroxide dissolves to a slight extent in water. It is also soluble in caustic alkali, from which solutions a black precipitate of finely divided ruthenium is obtained on addition of alcohol.\(^2\) Both the aqueous solution and the pure substance itself possess an odour resembling that of ozone. Its vapour, however, is not poisonous like that of the corresponding tetroxide of osmium. In contact with alcohol the solid tetroxide is reduced with explosive violence.\(^3\) When covered with water, to which a concentrated solution of caesium chloride is subsequently added and a little hydrochloric acid, ruthenium tetroxide is gradually converted into the oxy-salt Cs\(_2\)RuO\(_2\)Cl\(_4\). The corresponding rubidium salt has likewise been prepared.\(^4\)

Ruthenium tetroxide is permanent when kept in sealed tubes in the dry state and protected from light. Exposed to light it assumes a brown colour, but the brown product is soluble in alkali, yielding a ruthenate. Presumably the coloration is due to partial reduction. Owing to its ready reduction by organic substances whereby a black precipitate of finely divided ruthenium is obtained, potassium per-ruthenate has been found useful for histological microscopy.\(^5\)

Several other oxides have been described, namely, Ru\(_2\)O\(_5\),\(^2\) Ru\(_3\)O\(_5\).2H\(_2\)O,\(^2\) Ru\(_4\)O\(_5\),\(^2\) RuO\(_3\),\(^2\) \(^6\) and Ru\(_3\)O\(_7\).\(^2\) Of these, the first three are probably indefinite mixtures rather than separate chemical entities.\(^7\) The last two oxides do not appear capable of a separate existence although their compounds are well known. These are termed:

Ruthenates, M\(_2\)RuO\(_4\), and Per-ruthenates, MRuO\(_4\)

**Potassium Ruthenate**, K\(_2\)RuO\(_4\).H\(_2\)O, may be obtained by fusing ruthenium with a mixture of potassium hydroxide and nitrate. A green mass of potassium ruthenate is formed, which dissolves in water to an orange-coloured solution. It is also formed when 50 grams of ruthenium tetroxide are dissolved in 500 c.c. of water containing 70 grams of potassium hydroxide at 60° C. Crystals obtained by evaporation from its aqueous solution are rhombic in character, and possessed of a greenish metallic lustre. By transmitted light the crystals appear red. They absorb moisture from the air and darken owing to partial reduction. Heated to 200° C. they become anhydrous, but undergo no further change even at 440° C.

In solution potassium ruthenate is of a deep orange colour, but in dilute solution assumes a green colour, due to formation of per-ruthenate. Hydrochloric acid effects the precipitation of an oxide, chlorine being simultaneously evolved. The solution stains the skin black owing to separation of oxide.

The corresponding *sodium* derivative is readily prepared by fusing together ruthenium and sodium peroxide.\(^8\) The *silver, barium, strontium, calcium, and magnesium* salts are also known.

---

5. See Ranvier, *Compt. rend.*, 1887, 105, 146.  
Potassium Per-ruthenate, $\text{KRUO}_4\cdot\text{H}_2\text{O}$. This salt results by the action of chlorine on an aqueous solution of the normal ruthenate, as also by the solution of 50 grams of ruthenium tetroxide, previously fused under water, in 250 c.c. of water at $60^\circ$ $\text{C}$ containing 60 grams of potassium hydroxide.\(^1\) On crystallisation black tetragonal octahedra result, which, on heating in vacuo to $400^\circ$ $\text{C}$, decompose to oxygen, ruthenium dioxide, and potassium ruthenate.\(^2\) The crystals are not isomorphous with those of potassium permanganate\(^3\) as was at one time believed to be the case.

Sodium Per-ruthenate, $\text{NaRUO}_4\cdot\text{H}_2\text{O}$. is prepared in an analogous manner to the potassium salt as small, black, crystalline lamellae. It is considerably more soluble in water than the potassium analogue, and yields a dark green solution. Heated to $440^\circ$ $\text{C}$ water and oxygen are evolved.\(^4\)

RUTHENIUM AND SULPHUR

Ruthenium Sesquisulphide, $\text{Ru}_2\text{S}_3$, occurs in the platinum washings of Borneo and Oregon as the rare mineral laurite, usually in the form of minute octahedra; hardness 7-5, density 6-99. It has a bright metallic lustre and contains a little osmium. Deville and Debray\(^5\) prepared a similar sulphide artificially in the form of isometric crystals, octahedra, and cubes by heating ruthenium with pyrites and borax.

Ruthenium Disulphide, $\text{RuS}_2$, is formed by allowing hydrogen sulphide and potassium chlor-ruthenate solution to react at $80^\circ$ to $90^\circ$ $\text{C}$ when it is obtained as a black precipitate.\(^6\) When dry it explodes violently if warmed in air.

Ruthenium Tri sulphide, $\text{Ru}_3\text{S}_5$, is obtained by passing hydrogen sulphide through an aqueous solution of potassium chlor-ruthenate at $0^\circ$ $\text{C}$. It is formed as a yellowish brown precipitate. When dry it readily oxidises in air, becoming heated to incandescence; for this reason the sulphide is dried in an atmosphere of an inert gas.\(^7\)

Ruthenium Sesquisulphite, $\text{Ru}_3\text{SO}_4\cdot\text{H}_2\text{O}$, is obtained by passing sulphur dioxide through a solution of the sulphate whereby the colour changes from bright red through green to blue. Addition of alcohol precipitates the sulphite in a blue colloidal form which may be dried at $30^\circ$ $\text{C}$. It dissolves in excess of water, giving a solution from which it may be precipitated by addition of a salt. Double salts with the sulphites of potassium and sodium respectively have been prepared.\(^8\)

Thus, on boiling solutions of sodium chlor-ruthenite, $\text{Na}_4\text{RuCl}_5$, and sodium sulphite, a minute crystalline precipitate of sodium ruthenium sulphite, $\text{Na}_7\text{Ru(SO}_4)_2\cdot\text{H}_2\text{O}$, is obtained. The corresponding potassium salt has also been isolated. This, with potassium hydroxide solution is converted into the complex $\text{O[Ru(SO}_4)\text{Na}_2]_2\cdot\text{H}_2\text{O}$. The following salts have also been obtained, $\text{O[Ru(SO}_4)_2\text{(NO)}\text{Na}_2]_2\cdot\text{H}_2\text{O}$, and $\text{O[Ru(SO}_4)_2\text{(NO)}\text{K}_2]_2\cdot\text{H}_2\text{O}$, both in crystalline form.\(^8\)

\(^{1}\) Debray and Joly, Compt. rend., 1888, 106, 328; 1891, 113, 698.
\(^{2}\) Or possibly an allied substance.
\(^{4}\) Debray and Joly, Compt. rend., 1888, 106, 1494.
\(^{5}\) Deville and Debray, Bull. Soc. Min., 1879, 2, 185; Compt. rend., 1879, 89, 589.
\(^{6}\) Antony and Lucchesi, Gazzetta, 1900, 30, [ii], 589.
\(^{7}\) Claus, J. prakt. Chem., 1847, 42, 364; Antony and Lucchesi, Gazzetta, 1900, 30, [ii], 71.
\(^{8}\) Miolati and Tagluri, Gazzetta, 1900, 30, [ii], 511.
Ruthenium Dithionate, Ru$_2$O$_6$.—By the continued passage of sulphur dioxide through the sulphate solution the blue solution mentioned above becomes colourless, and ruthenium dithionate is produced in solution. It is precipitated from the solution as a yellowish white powder by addition of alcohol. On dissolving in water and concentrating, the salt is obtained as a yellow crystalline mass of radiating fibres. It is readily soluble in water and in acids. When warmed with permanganate solution ruthenium sulphate is produced.

Ruthenium Sulphate, Ru(SO$_4$)$_2$, results when the precipitated sulphide is oxidised by solution in nitric acid, and by dissolving barium ruthenate in fuming hydrochloric acid, evaporating to dryness, extracting with water and adding excess of dilute sulphuric acid. The barium is precipitated and the filtrate is concentrated, yielding a red liquid, from which, however, Antony could not obtain the crystalline salt. It is also produced by dissolving the tetroxide in sulphuric acid. On evaporation the orange solution yields a yellowish brown, amorphous residue, which is very deliquescent and easily soluble in water. On warming with alkalies, ruthenium hydroxide is precipitated from solution.

RUTHERNIIUM AND NITROGEN

Ruthenium Nitrosotrihydroxide, Ru(NO)(OH)$_3$, is readily obtained by addition of the requisite quantity of potassium hydroxide to a solution of potassium nitrosochlor-ruthenate, K$_2$Ru(NO)Cl$_5$, or 2KCl.Ru(NO)Cl$_3$, at the boiling-point.

$$2\text{KCl} \cdot \text{Ru(NO)Cl}_3 + 3\text{KOH} = 5\text{KCl} + \text{Ru(NO)(OH)}_3.$$  

The liquid, which had a reddish blue colour, becomes colourless, a clear brown, gelatinous precipitate of the hydroxide separating out. Since the hydroxide is soluble in excess of the potash, yielding a brown solution, care must be taken to add only the theoretical quantity required. Thorough washing with boiling water, in which the precipitate is insoluble, is desirable to remove all traces of potassium chloride.

When dissolved in potassium hydroxide solution and reduced with formaldehyde, a mixture of hydrates is obtained. Addition of hydrochloric acid and potassium chloride and subsequent evaporation results in brown crystals of potassium chlor-ruthenate, K$_2$RuCl$_9$, and red crystals of Ru$_2$(NO)Cl$_3$KCl.4HCl separating out. These differ in solubility, the former being more rapidly dissolved by cold water than the latter; the isolation of each in a pure state is thus easy.

When ruthenium nitrate is boiled with hydrochloric acid and evaporated at 120° C., a Nitrosochloride, RuCl$_3$.NO.H$_2$O, is obtained as a red crystalline mass. On recrystallisation a pentahydrate is formed, RuCl$_3$.NO.5H$_2$O, as dichroic triclinic crystals, which effloresce in dry air.

The nitrosochloride is also obtained by boiling for several days with aqua regia the precipitate formed on addition of dilute alcoholic potash to ruthenium tetroxide.

1 Antony and Lucchesi, Gazzetta, 1898, 28, [iii], 139.
2 Claus, Annalen, 1846, 59, 234.
3 Antony and Lucchesi, Gazzetta, 1899, 29, [ii], 312.
5 Howe, J. Amer. Chem. Soc., 1894, 16, 388. Absolute alcohol must not be employed on account of the explosive nature of the reaction. See p. 147.
Several other complex nitroso derivatives of ruthenium have been prepared, namely:

Ru₂(NO)₂(OH)Cl₂, Ru₂(NO)H₂(OH)₃, Ru₂(NO)H₂Cl₃·2HCl, and Ru₂(NO)H₂Cl₃·(NH₃)₅·2HCl;

but for accounts of these the reader is referred to the original memoir.¹

Ruthenium nitroso-tetribromide, Ru(NO)Br₄·H₂O, and tri-iodide, Ru(NO)I₅·Aq., have been described.²

Ammonio derivatives have also been prepared and are discussed in Volume X of this Series.

Potassium Nitrosochlor-ruthenate or Potassium Ruthenium Nitrosochloride, 2KCl·RuCl₃·NO or K₂RuCl₅NO, is obtained by direct precipitation of concentrated solutions of potassium chloride and ruthenium nitrosochloride; it also results on evaporation of mixed dilute solutions of the two substances.³ It yields black orthorhombic crystals which dissolve in water to a reddish violet solution. The aqueous solution is stable, its electric conductivity showing no alteration whatever after standing for two weeks. Its solution apparently contains three ions,⁴ namely, K⁺, K⁺, and RuCl₅·NO⁻.

This salt is interesting as being the one which led Claus in 1845 to identify ruthenium as a new element. He believed it to be K₂RuCl₅, analogous to potassium chlorplatinate, but Joly⁵ showed it to be a nitroso compound. The dihydrate, 2KCl·RuCl₃·NO·2H₂O, is deposited as black, efflorescent crystals when the mother-liquors of the salt are slowly concentrated.⁶

The corresponding bromine and iodine derivatives, namely, 2KBr·RuBr₃·NO and 2KI RuI₃·NO respectively, have been prepared.⁷

Ammonium Nitrosochlor-ruthenate,⁸

(NH₄)₂RuCl₅·NO or 2NH₄Cl·RuCl₃·NO,

and its dihydrate are prepared in a similar manner to the potassium salt, which it resembles. The bromine and iodine analogues have also been obtained.

Cesium Nitrosochlor-ruthenate, Cs₂RuCl₅·NO, and its dihydrate, Cs₂RuCl₅·NO·2H₂O are known.⁹

Rubidium Nitrosochlor-ruthenate, Rb₂RuCl₅·NO, is precipitated as a rather pale purple anhydrous salt on mixing concentrated solutions of rubidium chloride and ruthenium nitrosochloride.⁹ On recrystallisation from hot water very dark crystals are obtained.

If, however, dilute solutions of the above two compounds are mixed and evaporated over sulphuric acid the dihydrated salt, Rb₂RuCl₅·NO·2H₂O, separates out as large, dark purple crystals. These lose their water of crystallisation after further standing over concentrated sulphuric acid.⁹ The hydrated crystals are monoclinic and isomorphous with the corresponding cesium salt.

³ Howe, loc. cit.
¹⁰ N. D. Clarke, ibid., p. 395.
Double Nitrites

Potassium Ruthenium Nitrite, $4\text{KNO}_2 \cdot 2\text{Ru(NO}_2)_3$, is prepared by adding potassium nitrite to a dilute, acidified solution of ruthenium chloride at 60° C. until the solution just becomes alkaline. On concentrating slowly in the cold, orange-red crystals are obtained. With hydrochloric acid a nitroso derivative is obtained, whilst ammonium chloride decomposes it with evolution of nitrogen.

A basic salt, $8\text{KNO}_2 \cdot \text{Ru}_2\text{O} \cdot (\text{NO}_2)_4$, has also been isolated.

Sodium Ruthenium Nitrite, $4\text{NaNNO}_2 \cdot 2\text{Ru(NO}_2)_2 \cdot 2\text{H}_2\text{O}$, is obtained in an analogous manner to the potassium salt. It yields orange-yellow, dichroic crystals which are easily soluble in water. They effloresce upon exposure to air, and at 110° C. become anhydrous.

RUTHENIUM AND PHOSPHORUS

When spongy ruthenium is heated for five to six hours at 300° to 350° C. with phosphorus pentachloride and some phosphorus trichloride, a complex substance, known as tetrachlor diruthenium pentaphosphorus trichloride, $\text{Ru}_2\text{Cl}_{19}\text{P}_5$ or $2\text{RuCl}_2 \cdot 5\text{PCl}_3$, is obtained, and may be separated by means of chloroform, in dark, reddish yellow crystals. The following formula has been suggested as representing the constitution of this substance:

$$
\text{Cl} \quad \text{PCl}_3 \quad \text{Cl} \\
\text{Cl}_3\text{P} \cdot \text{Ru} \cdot \text{PCl}_3 \cdot \text{Ru} \cdot \text{PCl}_3 \\
\text{Cl} \quad \text{PCl}_3 \quad \text{Cl}
$$

The corresponding brom derivative, $\text{Ru}_2\text{Br}_{19}\text{P}_5$, has also been obtained.

RUTHENIUM AND CARBON

Carbides of ruthenium are not known.

Ruthenium Dicarbonyl, $\text{Ru(CO)}_2$—Ruthenium, like iron, yields a carbonyl derivative. It is obtained as an orange-yellow deposit upon subjecting ruthenium black to the action of carbon monoxide at 300° C. under a pressure of 400 atmospheres. The product is extracted from the residue by solution in alcohol. It is insoluble in benzene and in hydrochloric acid, but soluble in nitric acid and in bromine, gas being evolved. When heated, a mirror of metallic ruthenium is produced. In contradistinction to the other carbonyls of this group of metals ruthenium dicarbonyl is not volatile.

Potassium Ruthenocyanide, $K_4\text{Ru(CN)}_6 \cdot 3\text{H}_2\text{O}$, is obtained by heating to the point of fusion ammonium chlor-ruthenate with a slight excess of potassium cyanide for ten to fifteen minutes. Extraction of the melt with boiling water and subsequent evaporation yields crystals of potassium ruthenocyanide.

1 Dufet, loc. cit.; Joly and Vèzes, Compt. rend., 1889, 109, 667.
2 Joly and Leidi6, Compt. rend., 1894, 118, 468.
3 Dufet, loc. cit.
4 Strecker and Schurigin, Ber., 1909, 42, 1767.
6 Claus, Beiträge zur Chemie der Platinmetalle, 1854, p. 97.
Howe\(^1\) has prepared the salt in a variety of ways, the three yielding the best results were as follows:

1. Fusion of potassium ruthenium nitrosochloride with potassium cyanide. This gave a somewhat better yield than the method of Claus.

2. Ruthenium trichloride fused with potassium cyanide.

3. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, and thus containing potassium ruthenate, was dissolved in water and boiled with potassium cyanide. The orange colour was quickly bleached, the ruthenocyanide produced being subsequently isolated by crystallisation.

Potassium ruthenocyanide crystallises in square pseudo-rhombic plates, isomorphous with the corresponding ferro- and osmo-cyanides.\(^2\) Its solution in water yields no precipitate with salts of the alkaline earth metals as their ruthenocyanides are soluble. Ferric chloride gives a rich purple precipitate resembling Prussian blue in its chemical properties. Soluble in pure water it is precipitated by salts or alcohol. When precipitated in cotton fibre it adheres well, imparting its own beautiful colour. Alkalies decompose the salt, which, however, is re-formed on addition of dilute acid. This constitutes a useful test for ruthenocyanides.

Ferrous sulphate yields, with potassium ruthenocyanide, a pale blue precipitate which gradually oxidises to the purple one on standing, but instantly on addition of bromine.

With hydrochloric acid hydrogen cyanide is evolved on warming, and after a time a deep violet-blue precipitate of ruthenium cyanide with a little potassium cyanide is obtained. Chlorine colours the solution brownish yellow, possibly in consequence of the formation of a ruthenic cyanide, although no crystalline salt can be isolated from it.

**Barium Ruthenocyanide**, \(\text{Ba}_2\text{Ru(CN)}_6\cdot6\text{H}_2\text{O}\), may be prepared from the potassium salt as pale, straw-coloured monoclinic crystals. It is slightly soluble in cold water. When preserved over sulphuric acid the crystals lose water of crystallisation; at 100° C. 5·5 molecules are expelled, the remaining half molecule being retained up to nearly 200° C.\(^3\)

**Strontium Ruthenocyanide**, \(\text{Sr}_2\text{Ru(CN)}_6\cdot15\text{H}_2\text{O}\), has been prepared by decomposing the insoluble lead salt with sulphuric acid and neutralising the filtered hydrogen ruthenocyanide with strontium hydroxide.\(^4\) It crystallises in pale straw-coloured, elongated plates, probably monoclinic, and which readily dissolve in water. The corresponding strontium ferrocyanide likewise crystallises with 15 molecules of water.

The following ruthenocyanides have been obtained as precipitates by double decomposition with the potassium salt.\(^3\)

- **Lead**, white.
- **Silver**, white, curdy, insoluble both in ammonia and nitric acid.
- **Copper**, pale green, flocculent. Not brown, as given by Claus, whose product was probably contaminated with copper ferrocyanide.
- **Cadmium**, white, soluble in hot acid.
- **Zinc**, white.

---

2. Dufet, Compt. rend., 1895, 120, 377.
Tin, both stannous and stannic, white.
Mercury, white.
Bismuth, white, insoluble in nitric acid.
Nickel, dirty green, changing to blue with hydrochloric acid.
Cobalt, pale red.
Platinum, yellow-green.
Manganese, white, soluble in hydrochloric acid.

RUTHENIUM AND SILICON

Ruthenium Silicide, RuSi, results on heating a mixture of finely divided ruthenium and crystallised silicon in the electric furnace.\(^1\) The product is crushed and treated successively with alkali and a mixture of hydrofluoric and nitric acids. The silicide together with carborundum remains behind. The two may be separated with methylene iodide on account of the high density of ruthenium silicide, namely, 5.4.

Ruthenium silicide is a very hard, white substance, of great stability. It volatilises in the electric arc. Chlorine slowly attacks it, fluorine readily. It burns in oxygen at high temperatures, and is decomposed by sulphur vapour at red heat. Boiling acids do not affect it.

Detection and Estimation of Ruthenium.—See Chapter X.

\(^1\) Moissan and Manchot, Compt. rend., 1903, 137, 229.
CHAPTER V
RHODIUM AND ITS COMPOUNDS

RHODIUM
Symbol Rh. Atomic weight 102.9 (O = 16)

Occurrence and History.—Rhodium occurs as an alloy in platinum ore and osmiridium. An alloy with gold, known as rhodite or rhodium gold, contains from 30 to 48 per cent. of rhodium, and has a density of 15.5 to 16.8. The metal was discovered by Wollaston, and so named from the Greek ῥόδινος, a rose, in recognition of the colour of aqueous solutions of its salts.

Preparation.—Rhodium is obtained from platinum ores (see analyses, p. 258). The solution from which platinum has been precipitated as ammonium chlorplatinate is treated with metallic iron, which precipitates the more noble metals. The last-named residue is fused with a mixture of metallic lead and litharge. On cooling, the button of lead remaining is well cleaned, and contains metals less easily oxidised than itself, any others more readily oxidised being in the regulus and thus easily removed by mechanical means. Treatment of the metallic button with nitric acid effects the solution of lead, copper, and palladium. The insoluble portion containing the rhodium and other metals is fused with excess of barium dioxide, lixiviated with water and then treated with aqua regia. This effects the liberation of osmium, which can be recovered by distillation as explained on page 208; otherwise it may simply be boiled off in a fume-cupboard with a powerful draught, care being taken to avoid inhalation of the fumes, as these are exceedingly poisonous. When the odour of osmium has disappeared sufficient sulphuric acid is added to precipitate the barium. The filtrate is evaporated with a little nitric acid, and subsequently taken to dryness on the water-bath with excess of ammonium chloride. The residue is thoroughly washed with a concentrated solution of ammonium chloride (which effects the solution of the rhodium) until the wash waters cease to have an appreciable rose colour. The liquid is evaporated with an excess of nitric acid to destroy the ammonium chloride, the resulting rhodium salt is moistened with ammonium sulphide, mixed with excess of sulphur and heated to redness in a closed crucible. Metallic rhodium remains which may be further purified by successive prolonged boilings with aqua regia and concentrated sulphuric acid.

A still further purification of the rhodium is effected by fusing the metal obtained in the preceding manner to dull redness with metallic zinc, whereby the compound RhZn₂ is formed, with considerable heat evolution, a portion of the zinc being volatilised. On cooling, treatment of the mass with concentrated hydrochloric acid effects the solution of the excess of zinc, the insoluble crystalline alloy remaining unaffected.

2 Wollaston, Phil. Trans., 1804, p. 419.
The last named is dissolved in aqua regia, excess of ammonia added, and the solution evaporated to dryness, whereby the monochlor-rhodium pentamine chloride is formed. This is recrystallised to remove traces of iridium, calcined with sulphur in a crucible, and finally heated in the oxyhydrogen flame to volatilise any still remaining osmium.

**Properties.**—Rhodium is a white metal resembling aluminium in appearance. Its density has been variously given in values ranging from 11 to 12.1. It is a good conductor of heat and electricity, and its coefficient of linear expansion with rise of temperature is 0.04058.12

Rhodium melts at 1907° C. and boils at about 2500° C. It is less volatile than platinum, and when alloyed with that metal not only stiffens it, but, unlike iridium, reduces its volatility at all temperatures above 900° C. It has been suggested, therefore, that a useful alloy of better quality crucibles would consist of platinum 95 to 97 per cent., and rhodium 3 to 5 per cent., and containing no other detectable impurities. Below 900° C. the presence of rhodium appears to exert a negligible effect. When cooled to —80° C. rhodium appears to undergo a molecular transformation of some kind, analogous to that evidenced by copper. At this temperature the electrical resistance is considerably below the calculated value. The most intense lines in the spectrum of rhodium are as follows: 8


When rhodium is melted in the presence of charcoal some 7 per cent. of the carbon is dissolved, only to be thrown out again in the form of graphite on cooling. When heated in air the surface of the metal becomes slightly tarnished or oxidised.

Finely divided rhodium, such as that obtained by the reduction of its salts in hydrogen, is a greyish, porous powder which only absorbs small quantities of hydrogen, although it acts as a catalyst in promoting the union of hydrogen and oxygen. When heated strongly in air, oxygen is absorbed and the product, once believed to be rhodium monoxide, RhO, appears, from more recent research, to be an ill-defined mixture of metallic rhodium and its sesquioxide. The reaction is noticeable at 600° C., and increases in velocity with rise of temperature.
ture. At ordinary temperatures oxygen is without action upon rhodium. Chlorine attacks the finely divided metal, the reaction beginning at 250° C., yielding the trichloride, RhCl₃, which at high temperatures undergoes partial dissociation.

Bromine begins to react at the same temperature (250° C.), but the product has a variable composition, indicative of simultaneous dissociation. Thus:

\[ 2\text{Rh} + 3\text{Br}_2 \rightarrow 2\text{RhBr}_3 \]

Rhodium is insoluble in acids, even in aqua regia, although when its alloys are attacked by this latter mixture a portion of the rhodium passes into solution. When fused with potassium hydrogen sulphate, rhodium dissolves, yielding the sulphate. This reaction is interesting as affording a convenient method of separating the metal from iridium and platinum (see p. 344).

Rhodium that has been precipitated from solution evolves considerable quantities of various gases, such as carbon di-oxide, hydrogen, and oxygen, when heated in vacuo. After this treatment the metal does not occlude appreciable quantities of hydrogen or of carbon di-oxide between 420° C. and 1020° C.

Colloidal Rhodium may be prepared by Bredig’s method, which consists in sparking between rhodium electrodes submerged in ice-cooled water, a current of 2 amperes at 110 volts proving useful for the purpose. The solution has a reddish brown colour, and is very unstable.

Colloidal rhodium may also be prepared by reduction of pure rhodium salts with hydrazine hydrate. Traces of impurity prevent the formation of the hydrosol, which is very unstable. Addition of a protective colloid, such as a 1 per cent. solution of gum acacia, renders the hydrosol stable, so much so that it admits of concentration over sulphuric acid in vacuo, yielding a dark brown solid mass of colloidal metal, containing 99-4 per cent. of rhodium, and almost completely soluble in water. Shaking the colloidal solution with barium sulphate or animal charcoal serves to coagulate the metal.

Sodium protalbate or lysalbate may be used instead of gum acacia. Colloidal rhodium catalytically assists the decomposition of hydrogen peroxide in aqueous solution in a similar manner to colloidal platinum.

Colloidal rhodium prepared by Bredig’s method in the form of an unstable solution containing 0·002 gram of metal per litre is toxic towards pathogenic organisms, but has no poisonous action on fish, frogs, and dogs unless injected in large doses.

Explosive Rhodium.—In 1868 Bunsen accidentally discovered that several of the platinum metals can be obtained in an explosive form. Rhodium is a case in point. If alloyed with excess of zinc or cadmium, and the product treated with hydrochloric acid, the zinc (or cadmium) passes into solution, leaving an insoluble residue of finely divided explosive rhodium.

3 Sieverts and Jurisch, Ber., 1912, 45, 221.
6 Paal and Amberger, Ber., 1904, 37, 124.
7 Lancien, Compl. rend., 1911, 153, 1088.
8 Bunsen, Annalen, 1868, 146, 265.
Bunsen explained the explosive property of the metal on the assumption that an unstable modification or allotrope results from the above method of preparation, and that its conversion into the stable variety is accompanied by explosive violence. This view, however, is open to question. When explosive rhodium is kept at 100° to 200° C. for several days it ceases to be explosive. Furthermore, if the metal is obtained by the foregoing method in entire absence of air, it is not explosive.

This suggests that the explosiveness is due to the union of the occluded oxygen and hydrogen to form water, and not to an inherent change in the metal itself, a supposition which is supported by measurement of the amount of heat developed during explosion.\(^1\)

**Rhodium Black** is the name given to the black precipitate of indefinite composition obtained by reduction of solutions of rhodium salts, as, for example, by treatment with alcohol and potassium hydroxide or with a mixture of ammonium hydroxide, formate, and acetate. The precipitate consists of metallic rhodium associated with more or less hydride or oxide, and in an exceedingly fine state of subdivision.\(^2\) Inactive rhodium black becomes active after absorbing oxygen for a time.

For the preparation of rhodium black of permanent catalytic activity the presence of sulphur compounds appears to be necessary.\(^3\) Convenient methods of obtaining such consist in reducing rhodium sesquisulphide with formic acid; and by electrolytic deposition of rhodium black from a solution of rhodium in 60 per cent. sulphuric acid by a current of 0·02 ampere at 180° C.

Rhodium black dissolves not only in aqua regia, but also in concentrated sulphuric acid and in hydrochloric acid in the presence of air.\(^4\) It possesses powerful catalytic properties, decomposing formic acid into carbon dioxide and hydrogen at ordinary temperatures; alcoholic potash into potassium acetate and hydrogen; and liberating oxygen from solutions of alkali hypochlorites. The molecule of ozone is disrupted by rhodium black, yielding ordinary oxygen.

Precipitated rhodium, when heated in a vacuum, evolves a considerable volume of gas consisting of a mixture of carbon dioxide, oxygen, hydrogen, and water.\(^5\)

**Uses.**—Rhodium is used, both alone but generally alloyed with platinum, in the construction of scientific apparatus such as crucibles.\(^6\) A rhodium crucible is, for all practical purposes, as resistant as one of iridium, and is both cheaper and lighter.\(^7\) It has also found application in the manufacture of thermo-electric couples.\(^8\) Rhodium black has been used for producing a black colour in the decoration of porcelain.\(^9\)

**Atomic Weight.**—**Approximate Atomic Weight.**—That the atomic weight of rhodium is approximately 108 and not a multiple or fraction

---

5. Sieverts and Jursch, *Ber.*, 1912, 45, 221.
of this amount is evident from a variety of considerations. These may by summarised as follows:

1. According to Dulong and Petit’s Law the atomic weight of rhodium is of the order of 110, its specific heat being 0.058, and a mean atomic heat of 6.4 being assumed.

2. According to the Periodic Classification, rhodium, which in its properties forms a mean between cobalt and iridium, and between ruthenium and palladium, should have an atomic weight intermediate between the values for these extreme elements, namely, from 102 to 105.

3. Rhodium, like cobalt, iron, and aluminium, yields a well-defined series of alums. Application of Mitscherlich’s Law of Isomorphism indicates that these have the general formula:

\[ \text{M}_2\text{SO}_4\cdot\text{Rh}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}. \]

Analyses of these salts prove that the atomic weight of rhodium is approximately 103.

**Exact Atomic Weight.**—The earliest determinations of the atomic weight of rhodium, published by Berzelius in 1828, are now only of historical interest, his results, obtained from analyses of the sodium and potassium chlor-rhodites, \(\text{Na}_3\text{RhCl}_6\) and \(\text{K}_2\text{RhCl}_5\), varying from \(\text{Rh} = 103.1\) to \(\text{Rh} = 106.1\).

The first reasonably accurate determinations were those of Jörgensen in 1883, who reduced chloropentammine-rhodium dichloride,

\[ [\text{Rh(NH}_3)_5\text{Cl}]\text{Cl}_2, \]

and the corresponding bromine compound, \([\text{Rh(NH}_3)_5\text{Br}]\text{Br}_2\), to the metal by heating them in a stream of hydrogen. Subsequent experimenters, namely, Seubert and Kobbé, Hüttlinger, Dittmar, and Renz, have used the same two compounds. The results are as follow:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Result</th>
<th>Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Rh(NH}_3)_5\text{Cl}_2)</td>
<td>(\text{Rh} = 103.06)</td>
<td>4</td>
</tr>
<tr>
<td>(\text{Rh(NH}_3)_5\text{Br}_3)</td>
<td>(\text{Rh} = 102.97)</td>
<td>1</td>
</tr>
</tbody>
</table>

Jörgensen made one analysis of the bromine derivative for bromine, whilst Seubert and Kobbé made one estimation of chlorine in the other compound, the results being as follow:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Result</th>
<th>Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Rh(NH}_3)_5\text{Br}_3)</td>
<td>(\text{Rh} = 103.14)</td>
<td>3</td>
</tr>
<tr>
<td>(\text{Rh(NH}_3)_5\text{Cl}_2)</td>
<td>(\text{Rh} = 103.13)</td>
<td>2</td>
</tr>
</tbody>
</table>

7 The antecedent data used in the calculations in this section are as follow: \(\text{O} = 16.000\), \(\text{H} = 1.00762\), \(\text{N} = 14.008\), \(\text{Cl} = 35.457\), \(\text{Br} = 79.916\), \(\text{Ag} = 107.880\).
Rhodium and Its Compounds

The value accepted by the International Committee on Atomic Weights for 1918 is:

\[
\text{Rh} = 102.9,
\]

which, judging from the concordance between the preceding results, appears to be a close approximation to the correct value.

Alloys.—Rhodium does not alloy with silver. When added to molten silver it floats on the surface and is recovered, on cooling, in the amorphous condition.\(^1\)

It alloys with gold, an alloy, which probably contains a real compound, being obtained with 1 per cent. of rhodium, and which is entirely soluble in aqua regia. A 10 per cent. mixture yields free rhodium, on cooling, in the form of feathery crystals, whilst if still more rhodium is present, it separates as the amorphous metal.\(^2\)

Added to molten bismuth, a crystalline tetrabismuthide is formed,\(^3\) of composition corresponding to the formula RhBi\(_4\).

With tin, the compound RhSn\(_9\) is produced, which may be isolated from the melt by treating with diluted hydrochloric acid.

Rhodium dissolves in molten zinc at dull redness, and on treating the product with concentrated hydrochloric acid, the excess of zinc dissolves, leaving a crystalline powder of composition corresponding to the formula RhZn\(_2\). The formation of this insoluble alloy affords a convenient method of purifying rhodium (see p. 154).

Rhodium readily alloys with platinum, stiffening it and yielding mixtures that are useful for a variety of laboratory purposes. Rhodium reduces the loss in weight of platinum by volatilisation at all temperatures above 900° C., and it has therefore been suggested that a useful alloy for best quality crucibles “would be platinum containing 3 to 5 per cent. of rhodium, practically free from iron and iridium, and containing no other detectable impurities.” \(^2\)

Alloys containing less than 5 per cent. of rhodium are soluble in aqua regia. An alloy containing 30 per cent. of rhodium is insoluble in aqua regia, and is more readily fused than rhodium itself.\(^3\)

No compounds of platinum and rhodium\(^4\) appear to exist between the limits of 0 and 55 per cent. of rhodium.

Triple alloys, containing rhodium, iridium, and platinum are found in nature (see Platinum).

**Rhodium and Chlorine**

Rhodium Dichloride, RhCl\(_2\), is stated to result as a dull violet powder on passing chlorine over heated rhodium\(^5\) or rhodium monosulphide, RhS.\(^6\) Whether or not it is a separate chemical entity is uncertain,\(^7\) but the balance of evidence appears to be in favour of the assumption that it is not.

---

5. Bertzius, *vide infra*.
Insoluble Rhodium Trichloride, $\text{RhCl}_3$, may be obtained in a variety of ways:

1. By the action of chlorine at dull red heat. Berzelius observed that metallic rhodium, in a finely divided state, when heated to dull redness in chlorine absorbs some of the gas, yielding a product of empirical formula $\text{Rh}_2\text{Cl}_6$, which he regarded as a mixture of rhodium di- and tri-chlorides, $\text{RhCl}_2$ and $\text{RhCl}_3$. Claus,¹ however, concluded that neither $\text{Rh}_2\text{Cl}_6$ nor $\text{RhCl}_3$ could be obtained as a separate entity by this method, and that Berzelius' product was a mixture of rhodium trichloride and unattacked rhodium. Nevertheless, Claus himself was never able to cause rhodium under these conditions to take up the theoretical quantity of chlorine required for complete conversion of the metal into trichloride. Leidié ² many years later experienced the same difficulty both with finely divided metallic rhodium and with rhodium black. The latter gave decidedly the best results at red heat, the mean of three results being as follows:

<table>
<thead>
<tr>
<th></th>
<th>Found.</th>
<th>Calculated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodium</td>
<td>51.66</td>
<td>49.41</td>
</tr>
<tr>
<td>Chlorine</td>
<td>48.34</td>
<td>50.59</td>
</tr>
</tbody>
</table>

It appears probable, therefore, that rhodium trichloride undergoes partial dissociation at dull red heat, i.e. at about 550°C. The reaction between chlorine and finely divided rhodium begins ³ at about 250°C.

2. By prolonged heating of rhodium sesquisulphide in chlorine. It is exceedingly difficult, however, to expel the whole of the sulphur in this manner. Leidié ⁴ found that even after exposure to chlorine for eight hours at a dull red heat the product contained 0.81 per cent. of sulphur.

3. A convenient method of obtaining insoluble rhodium trichloride consists in heating its alloy with tin, namely, $\text{RhSn}_3$, to 440°C in a rapid current of chlorine gas. Air and moisture are first displaced by carbon dioxide; chlorine is then admitted and the temperature raised. The alloy is vigorously attacked, the tin escaping in the form of its volatile chloride, rhodium trichloride remaining behind.⁵ The product is cooled in chlorine, which is subsequently displaced by carbon dioxide. It is very important that both air and moisture should be excluded during the reaction, as otherwise complex oxy derivatives of tin are produced which are not volatile at the temperatures used, and incomplete separation of the metals occurs.

As obtained in this manner rhodium trichloride is a brick-red powder, insoluble alike in water and in acids.⁶

4. In a subsequent memoir Leidié ⁷ recommends the following method:

The anhydrous sodium, potassium, and ammonium chlor-rhodites (vide infra) on being heated in a current of pure, dry chlorine are decomposed into insoluble rhodium trichloride and the alkali chloride. The resulting mass is cooled in chlorine, which gas is finally replaced by dry carbon dioxide. If ammonium chlor-rhodite was employed initially the product now consists of pure rhodium trichloride, the ammonium

¹ Claus, opus cit., p. 63; J. prakt. Chem., 1860, 80, 282, 306.
⁴ Leidié, loc. cit.
⁵ Leidié, Compt. rend., 1899, 129, 1249.
The chloride having completely volatilised. If the sodium or potassium salt was employed, the product is extracted with water, the alkali salt dissolving, leaving the insoluble rhodium trichloride behind. As in this latter case a trace of alkali is liable to be left behind, it is preferable to use the ammonium salt.

(5) Finally, when soluble rhodium trichloride (vide infra) is heated to 440° C. in chlorine, it is converted into the insoluble salt.\(^1\)

Obtained by these methods rhodium trichloride is a red powder, insoluble in water and in acids. It is decomposed by concentrated aqueous potash, the resulting solution behaving like that of rhodium sesquioxides in the alkalis. It dissolves in concentrated solutions of potassium cyanide and of alkali oxalates, yielding complex cyanides and oxalates respectively.

When heated in chlorine with the chloride of an alkali metal, a double chloride or alkali chlor-rhodite is formed, which is soluble in water. Hydrogen reduces it at dull red heat to the pure metal, the reducing action taking place at temperatures as low as 190° C. with 'pure hydrogen'.\(^2\) It undergoes slight dissociation at high temperatures, and if heated in a current of chlorine to bright redness a slight formation of sublimate takes place, the composition of which varies slightly, but approximates to that required for the formula RhCl\(_3\).\(^3\) When raised to a bright red heat rhodium trichloride is gradually reduced to the metal.\(^4\)

**Soluble Rhodium Trichloride**, RhCl\(_3\).\(x\)H\(_2\)O, may be prepared by dissolving the hydrated sesquioxide in concentrated hydrochloric acid and evaporating. The product is not quite pure on account of the presence of alkali in the sesquioxide. Consequently it is advisable to extract with alcohol, which dissolves the rhodium salt, filter, evaporate, and recrystallise from water.

Leidie\(^5\) recommends the following method of preparation: Finely divided rhodium and excess of sodium chloride are heated to the fusion point of the latter in chlorine, and the resulting mixture of double chloride and excess sodium chloride dissolved in twice its weight of water. Concentrated hydrochloric acid is now added, and the whole allowed to stand twenty-four hours, whereby sodium chloride crystallises out. The solution is decanted, cooled to 0° C., and hydrogen chloride gas passed in. After saturation with the gas the containing vessel is sealed and kept for several days at 0° C., whereby the remaining excess of sodium chloride crystallises out. After decanting, the solution is gently evaporated until syrupy, and finally exposed over potassium hydroxide until all uncombined water has been removed.

The product is hydrated rhodium trichloride, which, according to Claus\(^6\) contains eight molecules of water. Leidie, on the other hand, concluded that the amount of water varies and does not correspond to any definite hydrate. It is an amorphous, brick-red, deliquescent substance which, on heating to 90–95° C., still retains four to five molecules of water and two of hydrogen chloride. At 100° C. it loses water and hydrogen chloride simultaneously, and at 175–180° C. it is completely dehydrated. At 360° C. it becomes insoluble in water, but it is most

---

4. Claus, *Beiträge*, etc., p. 64.
readily converted into the insoluble form by heating to 440 °C. in a current of chlorine.

Rhodium trichloride unites with chlorides of the alkali metals to yield two types of double salts, namely, the rhodohexachlorides or hexachlor-rhodites of general formula RhCl₃·3MCl or M₃RhCl₆, and the rhodopentachlorides or pentachlor-rhodites of general formula RhCl₅·2MCl or M₂RhCl₈, which correspond to the chlor-iridites and chlor-ruthenites respectively.

(A) Hexachlor-rhodites, M₃RhCl₆

These are isomorphous with the corresponding hexachlor-iridites.¹

Potassium Hexachlor-rhodite, K₃RhCl₆·aq., was stated by Claus ² to be formed on dissolving the hydrated sesquioxide in hydrochloric acid and adding a concentrated solution of potassium chloride. The yellow, acid solution becomes gradually red in colour, and in the course of a few weeks dark red, efflorescent crystals separate out. These were found to contain six molecules of water, of which three were readily lost on exposure to air.

Leidé ³ was not able to confirm the above, but succeeded in isolating what he believed to be the trihydrate, K₃RhCl₆·3H₂O, as the result ⁴ of decomposing potassium rhodium nitrite with warm hydrochloric acid, but which Duffour regards as the monohydrate, K₃RhCl₆·H₂O, isomorphous with the iridium analogue, K₃IrCl₆·H₂O.

Potassium chlor-rhodite is decomposed by water into potassium chloride and the double salt RhCl₃·2KCl, which is anhydrous and crystallises readily from aqueous solution. Owing to this ready decomposition, potassium chlor-rhodite cannot be prepared by simply mixing potassium and rhodium chlorides in solution.

When heated in dry hydrogen chloride gas, the water of crystallisation is liberated without the formation of rhodium sesquioxide, and the salt is transformed, slowly at 360 °C., but rapidly at 440 °C., into insoluble rhodium trichloride and potassium chloride. The latter may be dissolved away with hot water.

Sodium Hexachlor-rhodite, Na₃RhCl₆·18H₂O, is prepared by heating finely divided rhodium and sodium chloride to redness in a current of chlorine.⁵ Claus ⁶ recommends heating the rhodium in chlorine, cooling, adding the alkali chloride, and again heating in chlorine. There is then less danger of particles of rhodium remaining unattacked.

On extracting the product with water and evaporating, the salt crystallises out.

A more convenient method of preparation consists in warming sodium rhodium nitrite, 3NaNO₂·Rh(NO₂)₃, with concentrated hydrochloric acid.⁷ The salt crystallises in garnet-red octahedra, which effloresce on exposure to air. They are soluble in water, but not in alcohol. The amount of water of crystallisation has been a matter of dispute. Berzelius found 18H₂O, a result agreeing with that of Leidé ⁸ obtained many years later.

¹ Duffour, Compt. rend., 1912, 155, 222.
² Claus, Beiträge, etc., p. 21.
⁴ Leidé, Compt. rend., 1890, 111, 106.
⁵ Berzelius, Pogg. Annalen, 1828, 13, 437.
⁶ Claus, Beiträge, etc., p. 70.
⁷ Leidé, Compt. rend., 1890, 111, 106.
Ammonium Hexachlor-rhodite, \(2(\text{NH}_4)_2\text{RhCl}_6 \cdot 3\text{H}_2\text{O}\), may be prepared by mixing solutions of rhodium trichloride and ammonium chloride, the latter in excess. On slow evaporation in the cold, long red needles crystallise out.\(^1\)

The same salt is formed when ammonium rhodochlorinitrate, \(\text{RhCl}_4 \cdot 3\text{NH}_4\text{Cl} \cdot \text{NH}_2\text{NO}_3\), is decomposed with water and allowed to stand.\(^2\) In fact this is a better method of preparing the compound than the previous one, since there is no danger of its being contaminated with crystals of ammonium chloride.

Further, it is obtained on warming ammonium rhodium nitrite with concentrated hydrochloric acid.\(^3\) It is readily soluble in water, but not in alcohol. The crystals do not effloresce. When heated to glowing, metallic rhodium is left. According to Gutbier and Hüttlinger\(^4\) the salt may also be prepared by saturating an aqueous solution of potassium pentachlor-rhodite, \(\text{K}_2\text{RhCl}_5\), with hydrogen chloride, which affects the precipitation of most of the potassium chloride, and subsequently adding ammonium chloride. The salt separates on standing as dark red crystals.\(^5\)

(B) Pentachlor-rhodites, \(\text{M}_2\text{RhCl}_3\)

Ammonium Pentachlor-rhodite, \((\text{NH}_4)_2\text{RhCl}_5\)—This salt, associated with two molecules of water, was stated by Claus to result on boiling a solution of ammonium herachlor-rhodite. The monohydrated salt is prepared by concentrating a mixed solution of rhodium chloride and ammonium chloride in the theoretical quantities. It separates out in dark red crystals.

Caesium Pentachlor-rhodite, \(\text{Cs}_2\text{RhCl}_5 \cdot \text{H}_2\text{O}\), is obtained as a beautiful rose-coloured precipitate by concentrating mixed solutions of caesium chloride and potassium pentachlor-rhodite. It is also prepared by concentrating a mixed solution of caesium and rhodium chlorides in the requisite proportions.\(^7\)

Potassium Pentachlor-rhodite, \(\text{K}_2\text{RhCl}_5\), is obtained in the anhydrous condition when finely divided rhodium is heated to redness with potassium chloride in a current of chlorine (Berzelius).

The mass is extracted with water and crystallised. Berzelius suggested the formula \(\text{RhCl}_3 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}\), but Leidie\(^8\) was unable to confirm the presence of water. It seems probable, therefore, that Berzelius had obtained a mixture of salts.

Another method of preparing this salt consists in mixing solutions of rhodium trichloride and an excess of potassium chloride; on allowing to crystallise, the anhydrous salt, \(\text{K}_2\text{RhCl}_5\), separates out in orthorhombic crystals, of reddish colour, but slightly soluble in water and insoluble in alcohol.

\(^3\) Leidie, *Compt. rend.*, 1890, **IX**, 106.
\(^5\) Methyamine derivatives have been prepared. Vincent, *Compt. rend.*, 1885, **101**, 322; Friedel, *ibid.*, p. 322.
\(^7\) Gutbier and Hüttlinger, *loc. cit.*
The dihydrate of this salt, K₃RhCl₅·2H₂O, was stated by Claus to be formed on adding potassium chloride to a solution of sodium chlor-rhodite. It crystallises in small brown prisms which do not effloresce, and are rather difficultly soluble in water.

The monohydrate, K₃RhCl₅·H₂O, is obtained on fusing spongy rhodium with twice its weight of potassium chloride in a stream of chlorine. On cooling, the mass is extracted with water, and the solution, evaporated under reduced pressure, deposits deep red crystals of the monohydrated salt. If the mother-liquors are now saturated with hydrogen chloride to precipitate the excess of potassium chloride, and evaporated, dark red, sparingly soluble crystals of potassium chlor-rhodite, K₃RhCl₅·3H₂O, are obtained.

Rubidium Pentachlor-rhodite, Rb₂RhCl₅·H₂O, is prepared in a similar manner to the caesium salt (vide supra). It is formed as a red precipitate.

RHODIUM AND BROMINE

Rhodium Tribromide, RhBr₃.—Bromine begins to act on finely divided rhodium at about 250° C, but the product has an uncertain composition attributable to partial dissociation at the temperature of formation. Thus:

\[ \text{RhBr}_3 + \text{Br}_2 \rightarrow \text{RhBr}_5. \]

The dihydrate, RhBr₃·2H₂O, may be prepared by heating to 80° to 100° C. in a sealed tube spongy rhodium with 40 per cent. hydrobromic acid and a little bromine. The product is distilled under diminished pressure to remove excess of hydrobromic acid, the residue diluted with water and concentrated in vacuo over sulphuric acid, and finally over fused potash. The crystals obtained are blackish red in colour, and very soluble in water. At 100° to 140° C. they lose water and hydrogen bromide. With potassium hydroxide solution a basic salt is precipitated, namely, Rh(OH)₂Br·2H₂O, the solution containing potassium pentabromrhodite, K₃RhBr₅. By adding a slight excess of rhodium bromide solutions to those of alkali bromides, double salts are obtained. These have the general formula RhBr₃·2MBr or M₂RhBr₅, and are known as:

Pentabromrhodites or Rhodopentabromides.

Ammonium Pentabromrhodite, (NH₄)₂RhBr₅, is conveniently prepared by precipitating potassium bromide from a solution of potassium pentabromrhodite by passing in hydrogen bromide. To the filtrate dilute ammonium bromide solution is added. On standing for several days the salt separates out in blackish green crystals.

Cæsium Pentabromrhodite, Cs₂RhBr₅, results when a solution of the potassium salt is decomposed by addition of a concentrated solution of caesium bromide. The salt separates out as a green precipitate.

Potassium Pentabromrhodite, K₂RhBr₅, is obtained by heating finely divided rhodium with potassium bromide in a stream of bromine.

1 Claus, Beiträge, etc., p. 72.
5 A concentrated solution of ammonium bromide will not serve, probably because the rhodium derivative is soluble in it.
vapour. On cooling, the mass is extracted with water, and the filtered solution worked for crystals. These are obtained as small irregular leaflets, dark green in colour.

Rubidium Pentabromrhodite, Rb₂RhBr₅, has been prepared in a similar manner to the caesium salt. It has a darker green colour than the last named.

Sodium and Barium Pentabromrhodites have also been prepared.

RHODIUM AND IODINE

On adding a warm, concentrated solution of potassium iodide to one of rhodium bromide a black precipitate of Rhodium Tri-iodide, RhI₃, is obtained. Dilute solutions give no precipitate in the cold.

RHODIUM AND OXYGEN

At ordinary temperature oxygen has no action whatever upon rhodium, whether in the compact or the finely divided condition. Upon heating the finely divided metal in air oxygen is absorbed, the reaction being noticeable at 600° C. and proceeding with a greatly accelerated velocity at higher temperatures, as indicated in the following table:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1</td>
</tr>
<tr>
<td>700</td>
<td>30</td>
</tr>
<tr>
<td>800</td>
<td>70</td>
</tr>
<tr>
<td>1000</td>
<td>80</td>
</tr>
</tbody>
</table>

Analysis of the product obtained at high temperatures in air led both Berzelius and Wilm to conclude that an oxide of composition represented by the formula RhO is produced; but Claus adduced evidence in favour of the assumption that it is not a separate chemical entity, but a mixture of unoxidised metal and its sesquioxide. Leidé in 1889 repeated the experiments of former investigators, obtaining somewhat similar results. He wisely pointed out that these cannot be regarded as conclusive evidence either way, and for the present the existence of rhodium monoxide must be regarded as uncertain.

Tri-rhodium Tetroxide, Rh₃O₄, is obtained as a greyish black amorphous powder on heating the hydrated sesquioxide to redness. It is insoluble in acids and alkalies. Hydrogen reduces it to the metal at dull red heat.

Rhodium Sesquioxide, Rh₂O₃, results when rhodium is heated in air or oxygen between 600° C. and 1000° C. The rate of oxidation of the metal increases rapidly with the temperature. Above 1150° C. the oxide dissociates, metallic rhodium being obtained. The sesquioxide is greyish black in colour.

1 Gutbier and Hüttinger, Ber., 1908, 41, 210.
4 Wilm, Ber., 1882, 15, 2225.
5 Claus, Beiträge, etc., 1854, p. 64.
7 Leidé, loc. cit.
8 Gutbier, Hüttinger, and Maisch, Zeitseh. anorg. Chem., 1916, 95, 225; see also Leidé, loc. cit.
Hydrated Rhodium Sesquioxide, \( \text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \), is precipitated from solutions of rhodium salts, for example, rhodium trichloride, on addition of not too great a quantity of potassium or sodium hydroxide. On allowing to stand the red liquid deposits a rose-coloured precipitate consisting of the sesquioxide and some unaltered rhodium salt. The precipitate, however, gradually loses its red colour, becoming yellow, and remains such after thorough washing.\(^1\)

Obtained in the above manner rhodium sesquioxide is a yellow powder, and on being heated loses water and oxygen, yielding a black powder, which Claus regarded as the anhydrous sesquioxide, but for which Leidié's \(^2\) analyses suggest the empirical formula \( \text{Rh}_2\text{O}_4 \).

In the freshly precipitated condition rhodium sesquioxide dissolves in concentrated potassium hydroxide solution, from which it is precipitated again on dilution with water. If, however, chlorine is passed through the concentrated alkaline solution, a dark green precipitate of uncertain composition is formed, for which Claus suggested the formula \( \text{Rh}_2\text{O}_3 \cdot \text{Rh}_2\text{O}_2 \) or \( \text{Rh}_2\text{O}_5 \).

The sesquioxide readily dissolves in acids, giving yellow, non-crystalline salts of herbal taste.

Rhodium Dioxide, \( \text{RhO}_2 \), results in the anhydrous state on fusing a mixture of rhodium and potassium hydroxide and nitrate in a crucible heated to redness. The product is washed with water, then with hydrochloric acid, and finally dried at 100° C. in an inert gas such as carbon dioxide. It is a brown powder, insoluble in acids, in aqua regia, and even in boiling alkalies.\(^3\)

Hydrated Rhodium Dioxide, \( \text{RhO}_2 \cdot 2\text{H}_2\text{O} \) or \( \text{Rh(OH)}_4 \), has been obtained in a variety of ways.

(1) By passing chlorine into a solution of the freshly precipitated sesquioxides in concentrated potassium hydroxide solution.\(^4\) The reaction between the chlorine and potash causes the temperature to rise and the hydrated sesquioxide is precipitated, only to be oxidised by the hypochlorite in solution to the dioxide.

\[
2\text{KOH} + \text{Cl}_2 = \text{KCl} + \text{KClO} + \text{H}_2\text{O}
\]

\[
\text{KClO} + \text{Rh}_2\text{O}_3 = \text{KCl} + 2\text{RhO}_2,
\]

The precipitate is green, whilst the solution assumes a deep violet-blue colour, probably in consequence of the production of an alkali rhodate.

(2) Rhodium salts may be oxidised direct with alkali hypochlorites in alkaline solution to the dioxide. This has been effected with sodium chlor-rhodite,\(^5\) and with rhodium chloropurpureochloride.\(^6\)

(3) A green anodic deposit of dioxide is formed by electrolysing a double oxalate of rhodium and an alkali metal, or a double chloride in the presence of oxalic acid.\(^7\)

\(^1\) Claus, Beiträge zur Chemie der Platinmetalle, 1854, p. 67.
\(^3\) Berzelius (Schweigger's J., 1818, 23, 285) obtained by this method a grey-green product. Claus (Beiträge zur Chemie der Platinmetalle, 1854, p. 66) suggested that that colour was caused by the presence of traces of iridium as impurity in Berzelius' metal. Using very pure rhodium, Claus obtained a brown product the analyses of which agreed well with the formula \( \text{RhO}_2 \).
\(^4\) Claus, J. prakt. Chem., 1860, 80, 282; Beiträge, etc., p. 68.
\(^5\) Demargay, Compt. rend., 1885, 101, 961.
\(^6\) Jörgensen, J. prakt. Chem., 1883, 27, 446.
\(^7\) Joly and Leidié, Compt. rend., 1891, 112, 794.
The dioxide is insoluble in water, but dissolves in hydrochloric acid, yielding free chlorine and rhodium sesquisulphide.

The compounds $\text{K}_2\text{O} \cdot 6\text{RhO}_2$, $\text{Na}_2\text{O} \cdot 8\text{RhO}_2$, and $\text{BaO} \cdot 12\text{RhO}_2$ are obtained on heating to incipient redness the corresponding double nitrites. These are analogous to the cobaltites, chromites, and manganites, and prove that rhodium dioxide can exert an acidic action.

**Di-rhodium Pentoxide**, $\text{Rh}_2\text{O}_5$, was believed by Claus to be formed as a green precipitate on passing chlorine into a solution of the freshly precipitated sesquioxide in concentrated potash.

**Rhodium Trioxide**, $\text{Rh}_2\text{O}_3$, separates out as a blue precipitate from the solution left after preparing the dioxide (as indicated in (1) above), on neutralising the alkali with nitric acid. It dissolves in hydrochloric acid evolving chlorine, the trichloride remaining in solution:

$$2\text{RhO}_3 + 12\text{HCl} = 2\text{RhCl}_3 + 6\text{H}_2\text{O} + 3\text{Cl}_2.$$

**Sodium Rhodate**, $\text{Na}_2\text{RhO}_4$.—If the gases evolved by the action of hydrochloric acid upon potassium chlorate are passed into a solution of a rhodium salt rendered alkaline with sodium hydroxide, the liquid assumes a yellowish red, then a red colour, and finally a slight green precipitate forms. The latter dissolves, yielding a solution of blue colour known as Claus’s Blue, and containing sodium rhodate.

Sodium peroxide destroys the colour, as do also potassium persulphate and sulphur dioxide.

**RHODIUM AND SULPHUR**

**Rhodium Monosulphide**, $\text{RhS}$.—A product having an empirical composition corresponding to that required for rhodium monosulphide is produced:

(1) When rhodium is heated to dull redness in sulphur vapour. Combination takes place with incandescence. When the reaction has subsided any excess of sulphur is removed by heating in a neutral gas such as carbon dioxide.

(2) By raising to white heat a mixture of sulphur and ammonium chlor-rhodite; and,

(3) By fusing finely divided rhodium with iron pyrites. Treatment with hydrochloric acid leaves black, crystalline scales of rhodium sulphide. The sulphide may also be produced in the wet way by passing hydrogen sulphide into a solution of sodium chlor-rhodite, washing, and drying at an elevated temperature in a neutral gas. Leidié, however, gives reasons for believing that the various products obtained by the above methods are not simple chemical entities, but mixtures of rhodium and its sesquisulphide.

**Rhodium Sesquisulphide**, $\text{Rh}_2\text{S}_3$.—Two varieties of this sulphide are known, differing somewhat in their properties, yet apparently possessing the same chemical composition:

$\alpha$-**Variety.**—This variety results from “dry” methods of prepara-

tion, such as heating rhodium trichloride, prepared at 440° C., in a current of hydrogen sulphide at 360° C. In carrying out the operation it is essential that all the air should be expelled from the apparatus before heating, and that the hydrogen sulphide be entirely free from water and hydrogen chloride. The temperature during the course of the reaction should not exceed about 360° C., since at 400° C. the hydrogen sulphide partially dissociates, the hydrogen produced effecting the reduction of a portion of the chloride to metallic rhodium, which contaminates the final product. For the same reason hydrogen sulphide free from intermixed hydrogen is essential, and is best obtained by the action of hydrochloric acid on antimony sulphide. The reaction proceeds only slowly with rhodium trichloride prepared by the action of chlorine on the metal at dull redness; whilst ammonium chlor-rhodite gives unsatisfactory results, probably owing to the formation of alkali polysulphides that are volatilisable only with difficulty.¹

As obtained in this way rhodium sesquisulphide is a black, unctuous powder conserving the same crystalline form as the chloride from which it was prepared. It is not acted upon by acids, even aqua regia having no effect. Bromine and alkali sulphides are likewise without action on it.

When heated in an inert gas the sesquisulphide is stable up to above 500° C. At higher temperatures it loses sulphur, the resulting product varying in composition, but approaching that required for the monosulphide, Rh₅S. There is good reason to believe, however, that the product is really a mixture and not a definite monosulphide, although it is extremely difficult, if not indeed impossible, to remove the whole of the sulphur by heat. When heated strongly in air or oxygen, oxides of sulphur and rhodium are produced.

β-variety, produced by "wet" methods. To this end a rhodium salt, such as the trichloride, is decomposed by passing a current of hydrogen sulphide through its solution, which is then raised to and maintained at 100° C. Insufficient hydrogen sulphide should be added to precipitate the whole of the metal in the first case, since a sulphhydrate, Rh₃S₃.3H₂S, is formed, and this gradually decomposes at the higher temperature, the excess of metal in solution being precipitated by the hydrogen sulphide thereby liberated.²

Prepared in this manner, rhodium sesquisulphide is a black powder, insoluble in alkali sulphides, as also in nitric and hydrochloric acids, and even aqua regia at 100° C. Moist air is without action on it, as also is bromine.

**Rhodium Hydrogen Sulphide, Rhodium Sulphhydrate, Rh₅S₃.3H₂S.**

—When hydrogen sulphide is passed in excess into a solution of a rhodium salt, the sulphhydrate, Rh₃S₃.3H₂S, is formed as a black precipitate, slowly in the cold, rapidly on boiling. In the cold complete precipitation, particularly in the presence of excess of acid, may take several months. But given sufficient time for precipitation, whether in the cold or on boiling, the reaction is quantitative and the liquid becomes colourless. If only the theoretical quantity of hydrogen sulphide is added to precipitate the rhodium in solution, the same sulphhydrate appears first to form, and to decompose, very slowly in the cold,² more

---

¹ Leidié, loc. cit.
² Even after several days Leidié found the precipitate to have the empirical composition approximately represented by the formulas Rh₅S₃.2H₂S or 2Rh₃S₃.3H₂S.
rapidly on prolonged boiling, yielding the normal sesquisulphide, the hydrogen sulphide set free during decomposition effecting the precipitation of the remaining rhodium.

The same series of reactions appears to take place when the rhodium salt is in excess.¹

**Double Sulphides,** \( \text{Rh}_2\text{S}_3 \cdot 3\text{M}_2\text{S} \).—When a neutral rhodium salt, such as an alkali chlor-rhodite, is mixed with excess of an alkali sulphide, a precipitate is obtained which, on analysis, is found to contain a good deal of alkali sulphide. This suggests that a double sulphide has been formed. The precipitate, however, is stable only in the presence of excess of alkali sulphide, water rapidly decomposing it, so that direct isolation of the pure compound is not possible. By indirect physical methods, however, for details of which the reader is advised to consult the original memoir,¹ Leidié has obtained evidence of the existence of \( \text{Rh}_3\text{S}_4 \cdot 3\text{Na}_2\text{S} \), and apparently the corresponding potassium derivative is capable of existence.

**Rhodium Sulphite,** \( \text{Rh}_2(\text{SO}_3)_3 \cdot 6\text{H}_2\text{O} \), is obtained as a white crystalline mass on dissolving freshly precipitated rhodium sesquisulphide in sulphurous acid. On concentration the crystals separate out, and are washed with alcohol, in which they are insoluble. Rhodium sulphite is fairly stable, but evolves sulphur dioxide on heating, leaving a residue of sesquisulphide. With sulphites of the alkali metals, double salts are formed.²

**Rhodium Sulphate,** \( \text{Rh}_2(\text{SO}_4)_3 \), may be prepared by dissolving the sesquisulphide in sulphuric acid, and evaporating the solution to a syrupy consistence over a flame, finally expelling the excess of sulphuric acid at a temperature not exceeding 440° C. Obtained in this way, rhodium sulphate is a brick-red powder, which is not hygroscopic. It is not very soluble in water, by excess of which it is decomposed. When heated to 500° C. it begins to decompose.¹

**Basic Rhodium Sulphate.**—When the neutral rhodium sulphate is boiled with excess of water until the wash waters are not appreciably coloured, and cease to be acid towards indicators, a citron-yellow powder is obtained, insoluble in water. This is a basic sulphate, for which the formula \( \text{Rh}_2\text{SO}_9 \cdot 3\text{Rh}_2\text{SO}_4 \) is given by Leidié.¹

**Sodium Rhodium Sulphate,** \( \text{Na}_2\text{SO}_4 \cdot \text{Rh}_2\text{SO}_4 \), was first prepared by Bunsen³ by heating sodium rhodium sulphite with concentrated sulphuric acid. This salt was regarded by Seubert and Kobbe⁴ as an anhydrous rhodium alum. Since then, however, true rhodium alums have been obtained.

**Rhodium Alums,** \( \text{M}_2\text{SO}_4 \cdot \text{Rh}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O} \)

Rhodium sulphate, like its analogues the sulphates of cobalt and iridium, yields stable salts with sulphates of the alkali metals known as alums. These are well-defined crystalline salts, isomorphous with the better known iron and aluminium alums. They thus form an interesting link between these metals and the central vertical column in Group VIII, of which rhodium is the middle member. These alums

are obtained when a solution of rhodium sesquioxide in sulphuric acid is added to an alkali sulphate and allowed to crystallise. It is essential that excess of acid be present, and not more than about two-thirds of the theoretical quantity of alkali sulphate. The temperature must not be allowed to rise too high.

**Cesium Rhodium Alum**, Cs₂SO₄·Rh₂₃(SO₄)₂·24H₂O, is the most readily prepared of all the rhodium alums on account of its sparing solubility in cold water. The salt crystallises in small yellow octahedra which melt at 110° to 111° C. to a yellowish red liquid. When warmed in a desiccator it loses water, remaining yellow at 100° C., becoming yellowish red at 150° to 180° C., and brown up to 250° C., when it is almost entirely anhydrous.

This alum is of interest inasmuch as its formation renders it easy to separate rhodium from iridium. The sulphates of the metals, dissolved in acidulated water, are treated with cesium sulphate and evaporated. The rhodium alum crystallises out in a pure state, entirely free from iridium.¹

**Rubidium Rhodium Alum**, Rb₂SO₄·Rh₂₃(SO₄)₂·24H₂O, yields stable yellow crystals which melt at 108° to 109° C. to a bright red liquid.¹ The crystals belong to the regular system and exhibit a conchoidal fracture.

**Potassium Rhodium Alum**, K₂SO₄·Rh₂₃(SO₄)₂·24H₂O, can only be obtained in a crystalline state by allowing the solution to stand for a prolonged period at a temperature not exceeding 5° C. At higher temperatures a syrupy, uncrystallisable liquid results.¹

The crystals are light brown in colour, stable in air, but exceedingly soluble in water.

**Ammonium Rhodium Alum**, (NH₄)₂SO₄·Rh₂₃(SO₄)₂·24H₂O, yields orange-yellow crystals, readily soluble in water, although less so than the potassium salt. It readily yields large crystals. These are stable in air, melting at 102° to 105° C. to a brownish red liquid. When heated to redness, ammonia and sulphuric acid are expelled, leaving a residue of rhodium, contaminated with sulphate. The last named is not completely removed, even on reheating with ammonium carbonate.¹

**Thallium Rhodium Alum**, Tl₂SO₄·Rh₂₃(SO₄)₂·24H₂O, is somewhat difficult to prepare, partly on account of the small solubility of thallous sulphate. The alum is very soluble in water, and not altogether permanent in air, becoming converted into a whitish powder on prolonged exposure.¹

### RHODIUM AND NITROGEN

**Rhodium Nitrite** is not known, but double salts have been prepared.

**Rhodinitrites**, M₃Rh(NO₃)₆

**Potassium Rhodinitrite, Potassium Rhodium Nitrite**, K₃Rh(NO₃)₆ or 3KNO₃·Rh(NO₃)₃—are an acidified solution of rhodium chloride or the double potassium rhodium chloride, containing not more than 5 grams of rhodium per litre, is raised to boiling, and successive small additions of potassium nitrite added until the solution is bleached and a slight turbidity is produced. On cooling, the anhydrous potassium rhodium

Nitrite \(^1\) crystallises out, and may be dried at 105° C. The crystals are white, almost insoluble in cold water, quite insoluble in alcohol. On warming with concentrated hydrochloric acid it yields potassium hexachlor-rhodite, \(\text{K}_2\text{RhCl}_6\cdot3\text{H}_2\text{O}\). The insolubility of potassium rhodium nitrite may be made use of in the preparation of pure rhodium, as well as for its quantitative estimation. When heated to incipient redness until evolution of gas ceases, the product, \(\text{K}_2\text{O}\cdot6\text{RhO}_2\), is obtained.\(^2\)

**Sodium Rhodinitrite**, \(\text{Na}_3\text{Rh(NO}_3)_6\), is obtained in an analogous manner to the potassium salt, the original chloride solution containing about 40 grams of rhodium per litre.\(^1\) After adding the nitrate an equal volume of alcohol is added, which effects the precipitation of the salt, which may be recrystallised from water.

Sodium rhodinitrite dissolves in \(2\frac{1}{2}\) times its weight of water at 17° C., and in one part of boiling water. It is thus considerably more soluble than its potassium analogue. Its solution, however, does not give the reactions for rhodium, which suggests that it is a rhodinitrite, \(\text{Na}_3\text{Rh(NO}_3)_6\), analogous to potassium cobaltinitrite.

Hydrogen sulphide slowly precipitates from solution rhodium sulphide. Mineral acids attack it, slowly in the cold, rapidly on warming. Warm hydrochloric acid converts it into sodium chlor-rhodite (*vide supra*), \(\text{Na}_2\text{RhCl}_6\cdot18\text{H}_2\text{O}\). When heated to incipient redness until evolution of gas ceases, the compound \(\text{Na}_2\text{O}\cdot8\text{RhO}_2\) is obtained.

**Ammonium Rhodinitrite**, \((\text{NH}_4)_3\text{Rh(NO}_3)_6\), is best obtained by adding ammonium chloride to a solution of the sodium salt.\(^1\) With warm hydrochloric acid it yields ammonium chlor-rhodite, \((\text{NH}_4)_3\text{RhCl}_6\cdot6\text{H}_2\text{O}\).

The **Barium Salt**, \(\text{Ba}_3\text{Rh(NO}_3)_12\cdot12\text{H}_2\text{O}\), has also been prepared in an analogous manner to the sodium and potassium salts. It separates in somewhat bulky white crystals, which are soluble in water to the extent of one part in 50 of water at 16° C. and one part in 6:5 of water at the boiling-point. The crystals have no action on polarised light. With hydrochloric acid a mixture of barium and rhodium chlorides is obtained, and, by precipitating the barium with sulphuric acid, rhodium chloride can be obtained quite free from alkali chlorides.\(^1\)

**Rhodium Nitrate**, \(\text{Rh(NO}_3)_3\cdot2\text{H}_2\text{O}\), is prepared by dissolving rhodium sesquisoxide in nitric acid. On concentration it separates as a deep yellow hygroscopic salt, readily soluble in water, but not in alcohol. With nitrates of the alkali metals double salts are formed.

**Rhodium Uraninante**, \(\text{Rh(NO}_3)_3\cdot\text{UO}_2(\text{NO}_3)_2\cdot5\text{H}_2\text{O}\), has been obtained as orange leaflets which lose half of their combined water when kept in vacuo.\(^3\)

**Rhodium Ammonium Chlorinante** or **Ammonium Rhodichlor-nitrate**, \(\text{RhCl}_3\cdot3\text{NH}_4\text{Cl}\cdot\text{NH}_4\text{NO}_3\) or \((\text{NH}_4)_3\text{RhCl}_6(\text{NH}_4)\text{NO}_3\) may be obtained by adding a considerable excess of ammonium chloride and some nitric acid to a strongly acid solution of rhodium trichloride.\(^4\) It may also be prepared by addition of ammonium nitrate to an acid solution of ammonium chlor-rhodite.

On evaporation in a warm place the salt crystallises out in reddish

---

\(^1\) Leidié, *Compt. rend.*, 1890, **iii**, 106; *Bull. Soc. chim.*, 1891, 4, 809.

\(^2\) Joly and Leidié, *Compt. rend.*, 1898, 27, 103.


violet scales, resembling chromium trichloride. It was apparently first prepared by Claus as the result of crystallising a solution of ammonium chlor-rhodite in nitric acid. Claus, however, thought it was simply the chlor-rhodite in a second crystalline form. Wilm\(^1\) obtained the same salt, but overlooked its nitrate content, regarding it as a new double chloride, until Leidié drew attention to it.\(^2\)

Ammonium rhodochlorinate may be dried at 100-105\(^\circ\) C. without decomposition. It is very soluble in water, being decomposed by the same. The solution on standing deposits crystals of ammonium chlor-rhodite, and this is a useful method of preparing the latter salt free from excess of ammonium chloride. The rhodochlorinate is stable in solution or in the presence of aqua regia. It is but slightly soluble in nitric acid.

The formation of this salt, Leidié points out, may be taken advantage of in separating rhodium from other metals accompanying it during the treatment of platinum ores.

**RHODIUM, PHOSPHORUS, AND ARSENIC**

No definite phosphide of rhodium is known, although by reduction of rhodium basic phosphate with hydrogen, Claus obtained an indefinite mixture, possibly consisting of free metal associated with some phosphide.

On heating to dull redness a mixture of finely divided rhodium and phosphoric acid, a phosphate is obtained which is soluble in water.\(^3\) whilst a basic phosphate results on treating rhodium sesquioxide with phosphoric acid.

An arsenide of rhodium appears to be formed on fusing the two elements together,\(^4\) but it has not been definitely isolated.

**RHODIUM AND CARBON**

No definite carbide of rhodium is known, although when heated in the electric furnace in contact with carbon, rhodium dissolves some of the last named, the amount varying according to circumstances, as much as 7-88 per cent. being absorbed in five minutes with a current of 910 amperes and 50 volts. The presence of carbon renders the metal less malleable. When heated in chlorine the carbon is deposited from the mixture as graphite.\(^5\)

*Rhodium Cyanide*, \(\text{Rh(CN)}_3\), is obtained by decomposing potassium rhodicyanide with acetic acid, when it is precipitated as a red powder. It is soluble in potassium cyanide, and on heating to redness decomposes, yielding metallic rhodium. Acids attack it only with difficulty.\(^6\)

*Potassium Rhodicyanide*, \(\text{K}_2\text{Rh(CN)}_6\), may be obtained by heating ammonium chlor-rhodite with a slight excess of potassium cyanide to the fusion-point for ten to fifteen minutes,\(^7\) extraction of the melt with boiling water, and subsequent evaporation.

\(^1\) Wilm, *Ber.*, 1883, 16, 3033, 3039.
\(^3\) Fischer, *Pogg. Annalen*, 1830, 18, 257.
\(^4\) Wollaston, *Phil. Trans.*, 1829, 119, 1.
\(^5\) Moissan, *Compt. rend.*, 1896, 123, 16.
\(^7\) Claus, *Beiträge zur Chemie der Platinmetalle*, 1854, p. 96.
It may also be conveniently prepared by diluting with water a saturated solution of recently precipitated rhodium sesquioxide in 25 to 30 per cent. potash, until a precipitate begins to form, and pouring the whole into excess of a 20 to 25 per cent. solution of hydrocyanic acid. After standing some time out of contact with air, the liquid is filtered and evaporated in vacuo. The crystals separating out are isomorphous with those of the corresponding ferri-, cobalti- and iridi-cyanides. They possess similar optical properties and crystallographic angles.

When boiled with concentrated acetic acid, rhodium cyanide is precipitated, hydrogen cyanide escaping. Since the corresponding iridicyanide is not affected by similar treatment, this affords a useful method of separating rhodium from iridium.

Like the analogous ferri- and cobalti-cyanides it is decomposed by potassium hydroxide, and also by concentrated hydrochloric acid, in the latter case with evolution of hydrocyanic acid. With certain metallic salts it yields characteristic precipitates. Thus, with ferrous salts a white precipitate is obtained; with ferric, a bright yellow.

Detection and Estimation of Rhodium.—See Chapter X.

1 Leidie, Compt. rend., 1900, 130, 87.
CHAPTER VI

PALLADIUM AND ITS COMPOUNDS

PALLADIUM

Symbol, Pd. Atomic weight, 106.7 (O = 16)

Occurrence and History.—Palladium occurs native along with platinum in Brazil, St. Domingo, and the Urals. It is also found alloyed with gold as the mineral porpesite, the name being derived from Porpez in Brazil. Of this alloy the following may be taken as a typical analysis:

\[
\begin{array}{lll}
\text{Palladium} & . & . . . . \quad 8.21 \text{ per cent.} \\
\text{Gold} & . & . . . . \quad 91.06 \\
\text{Silver} & . & . . . . \quad \text{trace} \\
\text{Iron} & . & . . . . \quad " \\
\text{Density} & . & . . . . \quad 15.73
\end{array}
\]

The above proportions of palladium and gold correspond to the formula \( \text{PdAu}_8 \). A natural selenide of palladium, Eugenesite or selenopalladium, has been described as a silver-white, hard, crystalline alloy, which can be readily melted.

An important source of palladium is the nickeliferous ore of Sudbury, Ontario, from the matte of which it is isolated.

Palladium was discovered by Wollaston, and so named from the planet Pallas that had been discovered by his friend Olbers in 1802. Its presence in the sun’s photosphere has been demonstrated spectroscopically, and it has been found in a meteorite.

Preparation.—Metallic palladium is obtained by reduction of its salts. To this end ammonium chlor-palladite, \((\text{NH}_4)_2\text{PdCl}_4\), is very suitable. Upon ignition in hydrogen, ammonium chloride and hydrogen chloride volatilise, leaving the metal behind in a porous, spongy condition. In order to avoid occlusion of hydrogen the metal may be cooled in a current of carbon dioxide.

If the metal is required in a compact form, it may be fused in the oxyhydrogen flame, or simply raised to bright red heat and welded under pressure.

Several methods of separating palladium from the platinum metals are given in Chapter X. Of these an interesting one consists in precipitating the metal as iodide by addition of potassium iodide to a solution containing a soluble palladium salt. To obtain the free metal

4 Wollaston, Phil. Trans., 1804, p. 419; 1805, p. 316.
5 See Lockyer, Compt. rend., 1878, 86, 317.
6 Trottarelli, Gazzetta, 1890, 20, 611.
7 Addition of freshly precipitated silver iodide instead of potassium iodide is recommended by Orloff, Chem. Zeit., 1906, 30, 714.
the iodide is ignited in air, the last traces of iodine being removed by heating in a current of hydrogen. By this method Bunsen 1 isolated pure palladium from residues from the Russian Mint at Petrograd, the residues containing a mixture of all the platinum metals. A convenient method consists in precipitating palladium from solution as palladous cyanide by addition of mercuric cyanide. Palladous cyanide is insoluble in water and in dilute acids, and is the only cyanide of the platinum metals that can be thrown out in this manner. Upon ignition the salt decomposes, leaving a residue of metallic palladium.

Palladium may be obtained from porpesite or palladium-gold by fusion of the latter with silver, and digestion after granulation with dilute nitric acid. This effects the solution of the silver and palladium, metallic gold being left behind as residue. Addition of sodium chloride to the filtered solution precipitates the silver as chloride, and metallic palladium is obtained from the liquid by addition of metallic zinc.

Metallic palladium may also be prepared by precipitation from solutions of its salts with reducing agents such as formic acid or even strips of metallic zinc. It is thrown out in the finely divided condition, and may be rendered compact either by fusion or welding, as indicated above.

Pure Palladium may be prepared from the commercial foil 2 by dissolving in aqua regia and evaporating to dryness. The dichloride thus obtained is dissolved in water acidulated with hydrochloric acid, and the filtered solution treated with ammonia on the water-bath until the precipitate first formed has redissolved. Filtration removes iron, etc., but traces of copper may still remain, colouring the solution blue. To effect its removal, pure hydrogen chloride is passed into the solution, whereby the di-ammoniate or palladousammine, \( \text{PdCl}_2 \cdot 2\text{NH}_3 \), is precipitated. This is washed, redissolved in ammonia, and reprecipitated. By repeating this several times, all traces of iron, rhodium, copper, etc., are removed. The pure di-ammoniate is now reduced by ignition in hydrogen.

If traces of gold are suspected, the metal is now dissolved in aqua regia, repeatedly evaporated with hydrochloric acid to expel nitric acid, and the chloride dissolved in dilute hydrochloric acid. Pure sulphur dioxide is passed through the solution, and the whole allowed to stand. If there is no precipitate, gold is absent. When such is the case the chloride is converted into the di-ammoniate and reduced to the pure metal.

Physical Varieties of Palladium.—Palladium may be prepared in several different physical states, namely, as the ordinary compact metal, as colloidal metal, as palladium sponge, and finally as palladium black. Of these, the last named is not pure palladium, but an indefinite mixture in a state of very fine division. Each of these varieties has its own peculiar physical characteristics.

Physical Properties of Compact Palladium.—Palladium is a silvery-white metal, somewhat less ductile than platinum, but of equal or slightly greater hardness. It can be hammered into thin plates and drawn out into fine wire. It softens before reaching its melting-point, and can be welded below 1500° C. Its density is variously given,

1 Bunsen, *Phil. Mag.*, 1868, 36, 253.
depending upon its physical condition, the values ranging from 11,1
11.40 at 22.5° C.2 to 11.973 at 0° C. Hardness, 4-5 to 5.

Palladium melts at 1549-2° C.4 and boils at approximately 2540° C. It
can be distilled in the electric furnace.5 It is less volatile than
iridium, but more so than platinum.6 Its coefficient of linear expa-

sion with rise of temperature is 0.06176 between 0° and 100° C.7; its
specific heat between the same temperatures is 0.05928,8 and
between 0° and 1800° C. the value may be calculated from the

equation 9:

\[
\text{Specific Heat} = 0.0582 + 0.000010t.
\]

Molten palladium absorbs carbon, but on solidifying the latter
element is thrown out in the crystalline form as graphite.

The most intense lines in the spectrum of palladium are as follow10;

Arc: 3028-05, 3065-41, 3114-19, 3302-28, 3373-21, 3404-78,
3421-42, 3460-98, 3481-31, 3517-08, 3558-24, 3609-71, 3664-85,
3690-49, 3894-83, 3958-79, 4219-11, 5163-99, 5295-82, 5395-47,
5548-04, 5670-28, 6784-80.

Spark: 2776-95, 2854-70, 3404-80, 3421-41, 3481-34, 3517-11,
3558-21, 3609-70, 3634-83, 3894-39, 4218-16.

**Permeability to Hydrogen.**—Hydrogen readily diffuses through
palladium at temperatures ranging from 240° C. upwards. Graham11
illustrated this by means of a palladium tube composed of metal 1 mm.
in thickness, the tube measuring 115 mm. in length and 12 mm. in
internal diameter. It was closed by plates of platinum soldered at
both ends, one of the plates being perforated by a long narrow tube of
platinum, by which the cavity of the palladium tube could be exhausted
of air. The tube remained air-tight when exhausted, both at the
ordinary temperature, at 260° C., and at a temperature verging on low
redness, the external gas being air. When, however, the external gas
was hydrogen, although no gas appeared to pass through at 100° C.
hydrogen began to appear at 240° C., and more rapidly at 265° C.,
namely, at the rate of 327 c.c. per square metre per minute. At just
short of redness the rate increased to 428 c.c.

With coal-gas as external atmosphere Graham found that the
penetration began at about the same temperature, but the penetrating
gas appeared to be perfectly pure hydrogen, and contained no trace of
hydrocarbons. This was confirmed by Ramsay.12 Clearly it should be

---

1 Keiser and Breed, *loc. cit.*
3 Viole, *Compt. rend.*, 1878, 87, 981; 1879, 89, 702.
4 Day and Sosman, *Amer. J. Sci.*, 1910, [v], 29, 93. The constant volume nitrogen
thermometric scale was used. Other values obtained are 1535° C., 1540° C., and 1549° C.
(Holborn and Wien, *Wied. Annalen*, 1895, [ii], 56, 360), 1500° C. (Viole, *loc. cit.*).
5 Moisson, *Compt. rend.*, 1906, 142, 189.
270.
7 Fizeau, *Compt. rend.*, 1889, 68, 1125.
9 Viole, *loc. cit.*
10 Exner and Haschek, *Die Spektren der Elemente bei normalem Druck* (Leipzig and
Wien, 1911).
11 Graham, *Phil. Trans.*, 1866, 156, 399.
12 Ramsay, *Phil. Mag.*, 1894, 38, 266.
possible to test the percentage of hydrogen in coal-gas by this means, if the other constituents, as appears to be the case, are unable to pass through. The apparatus, however, will not retain its activity for very long; it is necessary to wash the coal gas with a solution of permanganate in order to free it from sulphur compounds. Since otherwise the palladium becomes coated with an impermeable layer of sulphide. Cyanogen, ether vapour, and marsh gas appear quite unable to pass through palladium.

Ramsay found that in all cases the partial pressure of the hydrogen which has diffused from outside into the interior of a palladium tube is lower than the pressure of the surrounding hydrogen no matter what inert gas is present within; although with nitrogen the discrepancy is at its maximum.

In order to explain the passage of hydrogen through palladium, Ramsay suggested that the gaseous molecule is split or dissociated, although he did not make it clear how such a change would facilitate the diffusion. The following year Hoitsema\(^1\) came to precisely the same conclusion for temperatures above 100° C., and this was supported by Winkelmann,\(^2\) who found that the quantity of hydrogen gas passing through a palladium septum does not diminish proportionally to the pressure, but that on the assumption that the hydrogen dissociates, and that the quantity of gas diffusing is proportional to the pressure of the dissociated molecules, an expression can be obtained which gives with reasonable accuracy the relation between the pressure in the apparatus and the quantity of gas diffusing.

The pressure-time curves, representing the diffusion of hydrogen through palladium at temperatures ranging from 100° to 300° C. under pressures of 700 to 100 mm. consist of two portions, which, it is concluded,\(^3\) correspond to the existence of two allotropic modifications of palladium. Generally speaking the rate of diffusion is proportional to the pressure of the gas. Below 100 mm. diffusion takes place more slowly, and the foregoing proportionality ceases to exist. The rate of diffusion under these conditions is apparently not related to any simple function of the pressure.

**Oclusion of Gases.**—Palladium possesses to a remarkable degree the power of absorbing or occluding certain gases, the actual extent of the absorption depending upon the physical condition of the metal. The term *occlusion* was first used by Graham in 1866\(^4\) to signify the absorption or shutting up of gases in solid substances.

Of all gases the most readily absorbed is hydrogen, and to this full reference is made below.

Both oxygen and carbon monoxide are absorbed by palladium black, the former presumably converting the metal into the monoxide, PdO, whilst the latter yields a curious substance which begins to decompose at 250° C.

Helium is not readily absorbed by palladium, a fact that enables admixed hydrogen to be readily separated from it.\(^5\)

---

1 Hoitsema, Zeitschr. physikal. Chem., 1895, 17, 1.
4 Graham, Phil. Trans., 1866, p. 399.
Occlusion of Hydrogen.—Palladium possesses to a remarkable extent the power of absorbing or occluding hydrogen, and numerous researches have been carried out by different investigators with a view to determining the condition of the occluded gas, and the influence it has upon the properties of palladium.

The absorption of hydrogen by palladium foil is readily shown by passing an electric current through acidulated water, using a platinum anode, but a plate of palladium, just previously heated to redness, as cathode. By using a narrow, vertical glass cell an image of the apparatus may be thrown on to a screen. Oxygen gas is evolved from the anode, but no gas evolution appears at the cathode, until the palladium has become saturated with gas, after which point hydrogen is evolved.

The first detailed researches on the subject are those of Graham, who experimented with thin palladium foil. He observed that palladium which has been ignited in vacuo absorbs large quantities of hydrogen at ordinary temperatures, rapidly yielding a large portion of the gas up again upon being placed in a vacuum, and slowly yielding it when exposed to air. The gas is rapidly and almost completely evolved in vacuo at 100°C. In experiments in which the foil was heated in hydrogen and allowed to cool in the gas, the metal absorbed 643 times its own volume of hydrogen, whilst in later experiments palladium wires absorbed over 900 times their volume of hydrogen. The occluded hydrogen was termed by Graham hydrogenium.

At its melting-point molten palladium absorbs less hydrogen than the solid metal, and consequently there is no "spitting" on solidification in an atmosphere of hydrogen.

Sieverts has studied the absorption of hydrogen from 138°C to 821°C and with varying pressures of gas ranging from 1 mm. to 760 mm. He observed that the amount of hydrogen absorbed per unit weight of palladium is nearly proportional to the square root of the hydrogen pressure.

The experimental results may be expressed by the equation:

$$L_p = k_1p^1 + k_2p,$$

in which $L_p$ is the quantity of hydrogen absorbed at pressure $p$, and $k_1$, $k_2$ are constants depending upon the temperature.

The expression is taken to represent that hydrogen molecules are in equilibrium with hydrogen atoms both in solution in the palladium and in the gaseous phase. Henry's Law appears to hold both for molecules and for atoms.

Graham showed that the density of palladium during hydrogenation undergoes a change, becoming considerably less, the volume of the whole undergoing appreciable expansion. In an experiment with palladium wire, which was made to absorb 936 times its volume of hydrogen, the density fell from 12.88 to 11.79, from which the density of the hydrogenium was estimated to be 1.708.

---

1 Newth, *Chemical Lecture Experiments* (Longmans, 1899).
2 Thomas (Zeitsch. physikal. Chem., 1889, 3, 69) has shown that palladium may even be supersaturated with hydrogen when charged electrically as above. The excess of gas, however, is evolved after the current ceases.
3 Graham, *Phil. Trans.*, 1866, 156, 399.
This change in volume of palladium during hydrogenation may be made the subject of a pretty lecture experiment. Two plates of palladium foil are varnished each on one side, and immersed in a cell containing acidulated water. On passing an electric current through, the electrode serving as cathode absorbs hydrogen on one side, expands and curls up, varnished side inwards, whilst the anode remains perpendicular. On reversing the current, the curled plate gradually straightens out, whilst the other plate begins to curl.

By using a narrow, vertical glass cell, the image may be thrown on to a screen, yielding a very effective demonstration.\(^1\)

Other physical properties of palladium are considerably modified by the absorption of hydrogen. For example, the electric conductivity falls continuously with increase of occluded hydrogen, becoming half its original value when the metal is saturated with the gas. At first, up to 40 volumes of hydrogen to one of palladium, the diminution in conductivity is directly proportional to the amount of occluded hydrogen; it then diminishes asymptotically until 600 volumes of gas have been absorbed, corresponding, according to Wolf, to the formation of a dihydride, \(\text{PdH}_2\), after which the further absorption of hydrogen results in a linear diminution in the conductivity once more.\(^2\)

The magnetic susceptibility of palladium is also diminished by hydrogen absorption.\(^3\) and if the diminution continues uniformly—which has not as yet been experimentally demonstrated—then palladium saturated with hydrogen should actually be diamagnetic.

The tensile strength of palladium is likewise reduced.\(^4\)

Alloying elements exert a very important influence upon the occlusion of hydrogen by palladium. The absorptive power of commercial palladium is from 10 to 20 per cent. less than that of the pure metal, a fact that is attributed to the presence of small quantities of platinum and ruthenium.\(^5\)

Silver and gold have an interesting influence. Addition of silver to palladium at first increases the solubility of hydrogen despite the fact that hydrogen is insoluble in pure silver. The maximum solubility is reached with 40 per cent. of silver, after which it falls. At 188° C. an alloy containing 40 per cent. of silver and 60 per cent. of palladium absorbs four times as much hydrogen as pure palladium. With 70 per cent. of silver the solubility of hydrogen is reduced to zero.

Gold behaves in an analogous manner, at first increasing and then decreasing the power of occluding hydrogen.\(^6\) In both cases the solubility of hydrogen is proportional to the square root of the pressure, and diminishes with rise of temperature.

Platinum in all proportions causes a reduction in the solubility of hydrogen in palladium, and although the solubility is, as in the preceding alloys, proportional to the square root of the gaseous pressure, it

\(^1\) Newth, loc. cit.


\(^4\) Graham, loc. cit.


does not diminish with rise of temperature—on the contrary, it increases.\(^1\)

The question now arises as to the condition of the hydrogen occluded by the metal. Is it chemically combined to yield a hydride or is it merely absorbed?

Troost and Hautefeuille\(^2\) considered that a hydride of formula \(\text{Pd}_2\text{H}\) was formed, and based their conclusions upon the results of a study of the tensions of hydrogen disengaged at various temperatures from hydrogenated palladium.

Graham,\(^3\) on the other hand, considered it "probable that the hydrogen enters palladium in the physical condition of liquid."

This theory of a mechanical absorption of hydrogen by palladium receives support from the researches of Hoitsema,\(^4\) who studied the

![Graph showing concentration of absorbed hydrogen]

variation in tension of hydrogen with the amount absorbed by the metal at different temperatures. If a definite compound is formed, then by reducing the volume of hydrogen in contact with the palladium no increase in pressure should be observed, only an increase in the amount of compound formed.

On plotting the hydrogen absorbed against the hydrogen pressure, the curves for different temperatures were found to assume the shapes indicated in Fig. 4, and consisted of three portions, namely, a preliminary rise of pressure with hydrogen content, followed by an almost stationary pressure with rise of absorbed hydrogen, and finally a further rise in pressure.

At first glance the horizontal portion of each curve appears to indicate the formation of a compound, but this is negated by the fact that the length of the central portion not only diminishes with

---

3 Graham, Phil. Trans., 1866, 156, 399.
4 Hoitsema, Zeitsch. physikal. Chem., 1895, 17, 1.
rise of temperature, but it does not end at the same concentration of hydrogen (A in the figure) as would otherwise be expected. It seems highly improbable, therefore, in view of these results, that a definite chemical compound of hydrogen and palladium is produced.

In further support of this may be cited the observation of Sieverts,\(^1\) that the quantity of hydrogen absorbed by unit weight of palladium is a function of the pressure and temperature only, and is quite independent of the superficial area of the metal. This would indicate that the absorption of hydrogen is an example of true solution rather than of definite chemical combination.

Occluded hydrogen is more reactive chemically than the normal gas. Hydrogenated palladium precipitates mercury and mercurous chloride from an aqueous solution of the dichloride, without any evolution of hydrogen. It reduces ferric salts to ferrous; potassium ferricyanide to ferrocyanide; chlorine water to hydrochloric acid; iodine water to hydriodic acid\(^2\); chromates to chrome salts; ceric to cerox salts; whilst cupric, stannic, arsenic, manganic, vanadic, and molybdic compounds are also partially reduced.\(^3\)

Ferric salts and potassium ferricyanide are completely reduced by charged palladium foil or wire, and the reduction may be carried out quantitatively if required for analytical purposes.

The reduction of a ferric salt to the ferrous condition may be demonstrated very effectively by an experiment described by Newth.\(^4\) A piece of palladium foil is charged with hydrogen by first heating to redness and then making it the cathode in a cell containing aciuluted water, through which an electric current is passing. When saturated with hydrogen the foil is withdrawn and immersed momentarily in a solution of ferric chloride. It is then dipped into a dilute solution of potassium ferricyanide, when the reduced ferrous chloride betrays its presence by yielding an immediate blue coloration.

It is interesting, in view of the foregoing reactions, to note that Hoitsema\(^5\) calculates that the hydrogen occluded by palladium, though at first it appears to be represented by \(H_2\), yet above 100\(^\circ\) C. it appears to be monatomic; and more recently Winkelmann\(^6\) has been led to the conclusion that hydrogen diffusing through palladium at high temperatures is dissociated (see p. 177). Although in both cases higher temperatures than atmospheric are postulated, the conclusions are interesting.

**Allotropy.**—An examination of the heating and cooling curves of palladium in vacuo and in hydrogen led Andrew and Holt\(^7\) to the conclusion that palladium is dimorphous, the stability of the two forms depending upon the temperature. The rate of change of the one form into the second is very slow, and the two forms do not absorb hydrogen with equal rapidity. This is borne out by a study of the rate of solution of hydrogen in palladium foil.\(^8\)

\(^{2}\) Graham, Phil. Trans., 1866, 156, 399; Proc. Roy. Soc., 1868-9, 17, 212.
\(^{3}\) Chapman, Analyst, 1904, 29, 346.
\(^{4}\) Newth, Chemical Lecture Experiments (Longmans, 1899).
\(^{5}\) Hoitsema, loc. cit.
\(^{6}\) Winkelmann, Ann. Physik, 1901, [iv], 6, 104.
The assumption that palladium can thus exist in allotropic forms receives interesting support from the work of Sieverts.\(^1\) This investigator points out that palladium black upon ignition yields palladium sponge, and that there is a simultaneous increase in the amount of hydrogen absorbed at temperatures below \(600^\circ\) C. Above this temperature the absorption of hydrogen by all physical varieties of palladium is practically the same. The explanation seems to be that both platinum black and sponge are mixtures of amorphous and crystalline palladium, the former of which has a greater power of absorbing hydrogen than the crystalline variety. On heating the palladium black, there is an alteration induced in the relative proportions of amorphous and crystalline metal, and consequently a variation in the amount of hydrogen absorbed is observed. Sieverts suggests that the absorption of hydrogen by the amorphous metal is a case of simple adsorption, whilst the hydrogen is actually dissolved in the crystalline variety.

**Chemical Properties.**—Both chlorine and fluorine attack palladium at high temperatures, yielding the respective halogenides. Chlorine water attacks it slowly, and an alcoholic solution of iodide effects the formation of a superficial layer of palladous iodide. Iodine vapour tarnishes the metal, yielding the iodide, whilst gently heating iodine and finely divided palladium causes them to unite more or less imperfectly.

Concentrated hydrochloric acid attacks the compact metal but slowly, whilst aqua regia rapidly effects its solution. Dilute nitric acid has but little action, although, when present in certain alloys, such as those with silver or copper, palladium will dissolve in it. Concentrated nitric acid readily attacks the metal. Boiling concentrated sulphuric acid converts it into palladous sulphate. Palladium is unique in that it displaces mercury from its cyanide.

When heated to dull redness in oxygen, the monoxide, \(\text{PdO}\), is formed, although at ordinary temperatures palladium is quite permanent in dry or moist air, and is not even attacked by ozone. On solidifying from the molten condition in an oxidising atmosphere, palladium “spits” just like silver. When heated in the oxyhydrogen flame it volatilises in greenish vapours.

Palladium, like rhodium, but unlike platinum, dissolves in fused potassium hydrogen sulphate, yielding palladous sulphate. Fusion with sodium peroxide converts it into palladium monoxide. Heated with sulphur combination takes place with incandescence.

Although closely resembling platinum in appearance, palladium is readily distinguished from the latter metal since an iodine solution upon evaporation in the warm produces a black stain on palladium but not on platinum.

**Catalytic Activity.**—Palladium is a powerful catalyser in each of its various physical varieties. The colloidal form is most active and its catalytic powers are discussed on page 184. Next comes palladium black (see p. 187), whilst finely divided palladium—as distinct from palladium black, which is not the pure metal—and compact palladium are also reactive.

**Catalytic Activity of Compact Palladium.**—Hydrogen combines with oxygen in the presence of palladium foil at \(280^\circ\) C., yielding water \(^2\); on

---

the other hand, hydrogenised palladium is without action on carbon monoxide or dioxide at the same temperature.

Ammonia is oxidised to oxides of nitrogen by means of oxygen in the presence of palladium foil heated to redness; and, as has already been pointed out, palladium foil saturated with hydrogen effects the reduction of ferric salts, chlorine water, iodine water, etc., to ferrous salts, hydrochloric acid, and hydriodic acid respectively. Hydrocarbons are oxidised to carbon dioxide and water when passed with air over palladium wire heated to redness. In the absence of air they are decomposed, yielding a deposit of carbon. After a time the palladium becomes brittle, and its surface, seen through a lens, resembles coke.\(^2\)

**Catalytic Activity of Finely Divided Palladium.**—Palladium may be obtained in a finely divided condition particularly suitable for catalytic action by pouring a solution of palladous chloride on to asbestos, adding a few drops of alcohol and igniting. By repeating the process until the asbestos increases some 6 per cent. in weight in consequence of the palladium, a very efficient catalyst is produced.\(^3\) It will effect the oxidation of hydrogen in the cold, although, be it remarked, hydrogen is the only combustible gas that admits of oxidation in this way without being heated. At bright red heat and in excess of air palladised asbestos will effect the complete oxidation of all hydrocarbons to carbon dioxide and water as efficiently as copper oxide. The employment of palladised asbestos has therefore been recommended for gas analysis.\(^4\) The paraffins are the most difficult to oxidise; acetylene and carbon monoxide come next, whilst the olefins are the most easily oxidised. Of the members of the same homologous series of hydrocarbons the lower are the more stable and offer greater resistance to oxidation.

The lowest temperatures at which oxidation of various substances was effected by palladised asbestos in the presence of air are given in the following table\(^5\):

<table>
<thead>
<tr>
<th>Substance</th>
<th>°C.</th>
<th>°C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>20</td>
<td>Benzene</td>
</tr>
<tr>
<td>Alcohol vapour</td>
<td>150</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>Pentane</td>
<td>170</td>
<td>Acetylene</td>
</tr>
<tr>
<td>Propylene</td>
<td>170</td>
<td>Propane</td>
</tr>
<tr>
<td>Ethylene</td>
<td>180</td>
<td>Methane</td>
</tr>
<tr>
<td>Isobutane</td>
<td>220</td>
<td>Ethane</td>
</tr>
</tbody>
</table>

Palladised copper oxide has also been used\(^6\) for a similar purpose, and for other catalytic reactions palladised metals have been tried. For example, the oxidation of sodium hypophosphite solution takes place according to the equation

\[
\text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} = \text{NaH}_2\text{PO}_3 + \text{H}_2
\]

through the agency of palladised copper or platinum, gaseous hydrogen

---

being evolved.\textsuperscript{1} A further oxidation to sodium phosphate also takes place, thus:

\[ \text{NaH}_2\text{PO}_3 + \text{H}_2\text{O} = \text{NaH}_2\text{PO}_4 + \text{H}_2. \]

The palladium deposit is found, however, to slowly lose its catalytic activity in a solution of the hypophosphite. Neither palladium foil nor palladium wire will exhibit catalytic activity in this reaction.

The amount of hypophosphite oxidised per unit time is proportional to the weight of catalyst present. Sodium hydroxide, hydrochloric and sulphuric acids, each retard the reaction, whilst the addition of sodium hydrogen carbonate either is without action or slightly enhances the velocity of reaction.\textsuperscript{2}

\textit{Palladous Salts} likewise possess catalytic properties. For example, they accelerate the oxidation of oxalic acid by persulphates, and, to a less extent, by nitric acid. This is attributable to the alternate formation of a palladic salt by the oxidiser and its reduction by the oxalic acid. Ammonia is likewise oxidised by persulphates in the presence of a palladous salt.\textsuperscript{3}

\textbf{Crystalline Palladium} was obtained by Joly\textsuperscript{4} as the result of heating palladium ribbon, dusted over with finely divided topaz, to redness by means of an electric current. The topaz apparently decomposes, evolving fluorine, which attacks the palladium, yielding a fluoride, which in turn dissociates, leaving a residue of crystalline metal. The crystals resemble those of platinum obtained in a similar manner both in colour and lustre, and appear also to be isomorphous with them.

\textbf{Palladium Hydrosol} or \textbf{Colloidal Palladium} is readily prepared by the reduction of the chloride with acrolein\textsuperscript{5} or with hydrazine hydrate, in either case in the presence of an extract of Iceland moss\textsuperscript{6} or in contact with sodium lysalbinate or protalbinate,\textsuperscript{7} gum acacia,\textsuperscript{8} or with lanolin\textsuperscript{9} in a precisely similar manner to platinum,\textsuperscript{10} the function of the organic additions, which are protective colloids, being to increase the stability of the colloidal phase.

Colloidal palladium may also be prepared by Bredig's method, which consists in sparking between palladium electrodes under ice-cooled water containing a little sodium hydroxide (approximately 0.04 grams NaOH per litre).\textsuperscript{11}

Palladium hydrosol is a brown or brownish black liquid in which the metallic particles are exceedingly small, as evidenced by the fact that a small portion will pass through a collodion filter that will retain dilute haemoglobin solutions. The colour of the filtrate is practically the same as that of the original liquid proportionately diluted, although it sometimes exhibits a slightly redder cast. Well-defined catalytic activity is manifested by dilute solutions containing only 0.0005 per

\textsuperscript{1} Sieverts and Peters, \textit{Zeitsch. physikal. Chem.}, 1916, 92, 199.
\textsuperscript{2} For experiments on the reduction of organic substances by palladium see Boeseken, \textit{Rec. trav. chim.}, 1916, 35, 260.
\textsuperscript{3} Scaglìarini and Berti-Ceroni, \textit{Gazzetta}, 1916, 46, ii, 51.
\textsuperscript{5} Castoro, \textit{Zeitsch. anorg. Chem.}, 1904, 41, 126.
\textsuperscript{6} Gutbier, Huber, and Kräuter, \textit{Kollod Zeitsch.}, 1916, 18, 65.
\textsuperscript{7} Paal, \textit{Ber.}, 1914, 47, 2202; 1904, 37, 124.
\textsuperscript{8} Gutbier and Hofmeier, \textit{J. prakt. Chem.}, 1905, 71, 358.
\textsuperscript{9} Amberger, \textit{Kollod. Zeitsch.}, 1913, 13, 310.
\textsuperscript{10} See p. 270.
\textsuperscript{11} Bredig and Fortner, \textit{Ber.}, 1904, 37, 798.
cent. of palladium, and such solutions have a detectable colour in layers of upwards of one centimetre in thickness.\(^1\)

Colloidal palladium catalytically assists the decomposition of aqueous solutions of hydrogen peroxide, oxygen being evolved. The reaction is monomolecular, and the influence of as minute a quantity of palladium as one gram atom in 26,000,000 litres of solution can be detected with N/60NaOH and N/10H\(_2\)O\(_2\) solution.\(^2\) The reaction is accelerated by the presence of caustic soda, the optimum concentration of which is about N/16. In acid solution the peroxide decomposes very slowly.

Colloidal palladium assists the combination of hydrogen and oxygen to form water. When excess of hydrogen is present the velocity of the reaction is greater than when the gases are in the exact proportion necessary to form water. On the other hand, excess of oxygen retards the velocity. In this respect colloidal palladium differs from colloidal platinum, the maximum velocity in this latter case being reached with the volume ratio: \(H:O = 2:1\).

It is reasonable to suppose that the great adsorptive power of palladium for hydrogen is the cause of this peculiarity.\(^3\)

By treating the pure hydrosol with hydrogen and measuring the amount of gas absorbed it has been observed\(^4\) that even with the same sample of colloidal palladium a considerable variation occurs, the amount varying from 926 to 2952 volumes of hydrogen per unit volume of metal. On heating the solution only a portion of the absorbed hydrogen is evolved. Why the whole of the gas is not liberated is not clear.

The activity of hydrogen is increased by absorption into palladium hydrosol. This was first observed\(^5\) in connection with the reduction of nitrobenzol in alcoholic solution, a quantity of aniline being produced by passing hydrogen through the solution after the addition of some palladium hydrosol. This is the more interesting inasmuch as neither palladium black nor palladium foil shares this property, and further, because aniline is a poison for catalysts, at any rate in small quantities, as Bredig first showed, although in larger amounts it exerts an accelerating action.

Comparison of the efficiencies of different colloidal metals may be established by determining the relative volumes of hydrogen used for reduction by them in unit time. This was effected by conducting hydrogen into a flask containing

\[
\begin{align*}
10 \text{ c.c. metallic hydrosol} \\
2 \text{ grams nitrobenzol} \\
10 \text{ c.c. alcohol}
\end{align*}
\]

and maintaining at 70° C.

The results indicate that there is but little to choose between platinum and palladium, but that iridium exerts a much less powerful activating influence, whilst that of osmium is very small. The actual figures obtained are:

---

\(^2\) Bredig and Fortner, Ber., 1904, 37, 798.
\(^3\) Paal and Hartmann, J. prakt. Chem., 1909, [ii], 80, 337.
\(^4\) Paal and Gerum, Ber., 1908, 41, 805.
\(^5\) Paal and Amberger, Ber., 1905, 38, 1406.
COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

Used 1 c c. of C.c. of hydrogen per hour.
Palladium hydrosol . . . . . . 12,000–82,000
Platinum , . . . . . . . . . . 6,700–57,000
Iridium , . . . . . . . . . . 2,000–4,000
Osmium , . . . . . . . . . . small action

The activity varies largely with the state of the colloid, as is to be expected. Old hydrosols appear to work more efficiently than samples freshly made. The temperature, too, exerts a most important influence.

In a similar manner to the foregoing, namely, by passing hydrogen gas through an alcoholic solution of the substance to be reduced, in the presence of palladium hydrosol, many other organic compounds have been exposed to the action of hydrogen. Of these not the least important are unsaturated vegetable oils such as linseed, olive, castor and cotton-seed, which are completely reduced, hydrogenated or hardened, yielding white solid oils or fats. These oils are now hydrogenated on a commercial scale, but finely divided nickel or its oxide is usually employed as catalyst (see p. 93).

Like that of platinum, palladium hydrosol is affected by poisons, hydrogen sulphide, mercuric chloride, hydrogen cyanide, and hydrogen arsenide exerting a marked retarding influence. For example, the addition of N/107 iodine to N/13200 palladium reduces the velocity of decomposition of hydrogen peroxide by colloidal palladium by 25 per cent. Hydrogen sulphide probably retards the reaction by converting the palladium into sulphide.

Colloidal palladium exerts a remarkable absorptive power on acetylene, some 5000 times its volume of the gas being occluded. The reaction continues for several days, proceeding rapidly at first, and then gradually slowing down. The absorption is facilitated by slight increase in pressure, and also by raising the temperature. Upon exposure to air, only part of the acetylene is evolved, and only a small amount is absorbed again upon further exposure to acetylene. It is generally assumed that polymerides or condensation products are formed.

Colloidal palladium oxidises solutions of sodium dihydrogen hypophosphite to phosphite and phosphate in the same manner as the electrolytically deposited metal and palladium black (see p. 188), but the activity of the colloidal metal is greater.

Colloidal palladium converts mercury and mercuric oxide into colloidal solution, and thereby loses its own catalytic activity. It is suggested that possibly a hydrosol of palladium amalgam is formed.

Palladium hydrosol may be obtained in the solid condition by concentration of the aqueous solution, containing a protective colloid such as gum acacia, by exposure over sulphuric acid in vacuo. It has also been prepared by passage of hydrogen through a solution of palladium chloride at 60° C. in the presence of sodium protalbate. After dialysis the solution is evaporated on the water-bath, and dried as before in vacuo over sulphuric acid.

1 Paal and Roth, Ber., 1908, 41, 2282; 1909, 42, 1541.
2 Bredig and Fortner, loc. cit.
3 Paal and Hohenegger, Ber., 1910, 43, 2084; 1915, 48, 257; Paal and Schwarz, Ber., 1915, 48, 1195.
4 Paal and Hartmann, Ber., 1918, 51, 711.
5 Gutbier and Hofmeier, loc. cit.
6 Paal and Amberger, Ber., 1905, 38, 1398.
The solid hydrosol readily dissolves in water again to yield a colloidal solution. When warmed to 60° or 110° C. in hydrogen the solid hydrosol absorbs the gas, but yields it up again when raised to 180° or 140° C. in an atmosphere of carbon dioxide, at which temperature the protective colloid (sodium lysalbate) is still undecomposed.

**Spongy Palladium** is readily obtained by heating ammonium chloropalladite, \( (\text{NH}_4)_{2}\text{PdCl}_4 \), in hydrogen. It is then in a particularly suitable condition for exhibiting catalytic activity. Graham prepared it by ignition of the cyanide, and Berry by reduction of the chloride with sodium formate in hot aqueous solution.

When spongy palladium is exposed to an atmosphere of hydrogen gas at temperatures ranging from \(-50° \text{ C.}\) upwards it occludes hydrogen, the mass becoming pyrophoric. The amount of occluded gas steadily decreases from 917 volumes to one of palladium at \(-50° \text{ C.}\) to a minimum of 661 volumes at \(+20° \text{ C.}\). It then rises again to 754 volumes at 105° C.4

At very low temperatures, such as those of liquid air, palladium sponge has an extremely large capacity for hydrogen, and palladium sponge at \(-190° \text{ C.}\) has therefore been recommended as a convenient substance for removing the last traces of hydrogen from other gases.

The chemical activity of the absorbed hydrogen is considerably enhanced. For example, the hydrogenated sponge when placed for twenty-four hours in the dark at ordinary temperatures in dilute solutions of ferric salts reduces them to the ferrous condition. In a similar manner potassium ferrocyanide is reduced to ferrocyanide; chlorine water to hydrochloric acid; and iodine water to hydriodic acid.

Graham also found palladium sponge to exhibit a selective absorption for alcohol in preference to water, a power not manifested either by platinum sponge or by spongy iron. For example, palladium sponge was left in contact with a mixture of alcohol and water in a sealed tube for two days. At the expiration of this time the supernatant liquid was removed and found to contain less alcohol, whilst the portion retained by the palladium contained more alcohol in proportion than the original mixture.

**Palladium Black** is not pure palladium, but an indefinite mixture in a very high state of fine subdivision, obtained by precipitation from solutions of palladium salts with reducing agents such as sodium formate.

Obtained by reduction with sodium formate, Mond found palladium black to contain 1:65 per cent. of oxygen, which, however, cannot be removed in vacuo even at a dull red heat, and must therefore be estimated by reduction with hydrogen and weighing the water formed.

Dried at 100° C. palladium black contains 0:72 per cent. of water, and hence, assuming the oxygen exists as palladium monoxide, the composition of the black is as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>86:59 per cent.</td>
</tr>
<tr>
<td>PdO</td>
<td>12:69 &quot;</td>
</tr>
<tr>
<td>H₂O</td>
<td>0:72 &quot;</td>
</tr>
</tbody>
</table>

1 Peal and Amberger, Ber., 1905, 38, 1398.
2 Graham, Phil. Trans., 1866, 155, 399.
4 Gebhardt, and Ottenstein, Ber., 1913, 46, 1453.
6 See Platinum Black, p. 273.
When ignited in oxygen palladium black absorbs the gas up to a red heat, yielding a brownish black substance that does not yield up its gas at red heat in vacuo, the inference being that the free metal is thereby converted into the monoxide. When exposed to hydrogen 1100 volumes of gas are absorbed, the bulk being occluded, the remainder serving to reduce the monoxide. Of the occluded hydrogen, 92 per cent. can be slowly regained by pumping at the ordinary temperature, and practically all the remainder upon heating to 444° C.

The heat evolved on the occlusion of hydrogen by palladium black is nearly the same as that evolved by platinum black under similar conditions. The heat of occlusion remains constant for the different fractions of hydrogen occluded, namely, 4640 calories per gram of hydrogen, or 4870 calories if the external work done by the atmosphere is allowed for.

Palladium black when heated in hydrogen readily absorbs the gas which it evolves on heating, one volume of the metal evolving 67½ times its volume of hydrogen.

When suspended in water palladium black absorbs even more hydrogen, namely, in one case 1204 times its own volume. Under similar conditions it likewise absorbs acetylene slowly; when suspended in 60 per cent. alcohol it has a pronounced adsorptive action, as also when suspended in an aqueous solution of sodium protoalinate. The absorbed acetylene exhibits an enhanced chemical activity. The curves obtained by plotting the rate of absorption of hydrogen by platinum black are smooth, indicating that only one allotropic form of palladium is present.

Palladium black catalytically assists the oxidation of sodium dihydrogen hypophosphite solution to sodium phosphite, thus:

\[
NaH_2PO_2 + H_2O = NaH_2PO_3 + H_2, \]

hydrogen gas being evolved. The reaction proceeds even further, the phosphite being oxidised to phosphate:

\[
NaH_2PO_4 + H_2O = NaH_2PO_4 + H_2. \]

Palladium black slowly absorbs 36 times its volume of carbon monoxide at ordinary temperature, and appears to form a chemical compound with it, although efforts to isolate such have proved abortive. It can hardly be purely mechanical absorption of the gas, since other gases such as hydrogen do not effect its elimination. Upon heating to 520° C. the carbon monoxide is suddenly liberated.

Uses.—Palladium is seldom used in the pure state, and its alloys have hitherto received but little application even in scientific work, although recently a useful field has been discovered for utilising certain alloys, such as those of palladium and gold, as substitutes for platinum. They have been used, on account of their excellent resistance to atmospheric corrosion, for certain astronomical and dental purposes, and for coating the surfaces of reflectors used for searchlights, etc. Palladium salts are used in photography.

Atomic Weight.—Approximate Atomic Weight.—That the atomic

2 Paal and Amberger, Ber., 1905, 38, 1394.
3 Paal and Gerum, Ber., 1908, 41, 818.
4 Paal and Hohenegger, Ber., 1913, 46, 128; 1910, 43, 2092.
The atomic weight of palladium is approximately 107, and not a multiple or fraction of this amount, is clearly indicated by several considerations. Chief amongst these are:

1. The specific heat of palladium is 0.059; assuming, therefore, a mean atomic heat of 6.4, the atomic weight of the metal, according to Dulong and Petit's Law, is approximately 108.

2. A study of the chemical properties of palladium and its compounds reveals a close analogy, as explained in Chapter I, between this element and nickel and platinum. Furthermore, a more or less regular gradation in properties can be traced as we compare ruthenium with rhodium, and rhodium with palladium. These facts suggest that palladium should be placed at the end of one of the triads of Group VIII in the same vertical line as nickel and platinum. At present there is only one such vacancy, namely, that next to rhodium, and besetting an element of atomic weight lying between 102.9 (atomic weight of rhodium) and 107.88 (atomic weight of silver).

3. Alkali chlor-palladites and chlor-palladates are isomorphous with the corresponding chlor-platinates and chlor-platinumates. Application of Mitscherlich's Law of Isomorphism leads to the conclusion that these salts have a similar constitution, and are therefore represented by the general formulae $M_2PdCl_4$ and $M_2PdCl_6$, assuming those for the platinum derivatives to be $M_2PtCl_4$ and $M_2PtCl_6$ respectively.

Analyses of these compounds indicate that the atomic weight of palladium is 106.7.

**Exact Atomic Weight.**—The first determinations of the atomic weight of palladium were made by Berzelius. His analysis of palladium monosulphide $^1$ is of no present value; and the same remark applies to his analyses of potassium chlor-palladite, $K_2PdCl_4$, although until the year 1889 the accepted value for the atomic weight of palladium was based upon the results. Berzelius $^2$ decomposed the salt by ignition in a stream of hydrogen, determining the loss in weight and the amounts of palladium and potassium chloride in the residue. His results lead to values for the atomic weight of palladium varying from 104.9 to 111.1, probably because the double salt was incompletely dried; his ratio $Pd:2KCl$, which is independent of this source of error, leads to the value $Pd = 106.2$. $^3$

The first modern determination of the atomic weight of palladium was published by Keiser in 1889. $^4$ This chemist considered that palladosammine chloride, $Pd(NH_3)_2Cl_2$, was the most suitable palladium compound for atomic weight work, and most subsequent experimenters have utilised this compound or the corresponding bromide. Keiser analysed the compound for palladium by heating it in a stream of pure, dry hydrogen, and this method has also been employed by Bailey and Lamb, $^5$ Keller and Smith, $^6$ Keiser and Breed, $^7$ Krell, $^8$ Woernle, $^9$ and others.

---

3. The antecedent data used in all the calculations in this section are as follow: $O = 16.000$, $H = 1.00762$, $N = 14.008$, $Cl = 35.457$, $Br = 79.916$, $Ag = 107.880$, $K = 39.100$, $C = 12.003$. $^4$ Keiser, *Amer. Chem. J.*, 1889, 11, 398.
Kemmerer.\(^1\) On the other hand, Keller and Smith, who consider that traces of palladium are lost by this method, determined the palladium content of the compound electrolytically, as also did Amberg\(^2\) in two series of experiments, and Woernle. Moreover, Amberg made a series of determinations in which the reduction to metal was accomplished in solution with hydrazine sulphate, while Shinn\(^3\) effected his reductions with ammonium formate. The results of these investigations are summarised in the following table:

\[
\text{Pd(NH}_3\text{)}_2\text{Cl}_2 : \text{Pd} : : 100-000 : x
\]

<table>
<thead>
<tr>
<th>Date</th>
<th>Experimenter</th>
<th>No. of Expts</th>
<th>Value of (x)</th>
<th>Atomic Weight of Palladium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1889</td>
<td>Keiser (i)</td>
<td>11</td>
<td>50·360</td>
<td>106·50</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>8</td>
<td>50·359</td>
<td>106·49</td>
</tr>
<tr>
<td>1892</td>
<td>Bailey and Lamb</td>
<td>10</td>
<td>50·171</td>
<td>105·70</td>
</tr>
<tr>
<td>1892</td>
<td>Keller and Smith</td>
<td>14</td>
<td>50·388</td>
<td>106·62</td>
</tr>
<tr>
<td>1894</td>
<td>Keiser and Breed</td>
<td>5</td>
<td>50·351</td>
<td>106·46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>50·382</td>
<td>106·46</td>
</tr>
<tr>
<td>1906</td>
<td>Keless</td>
<td>5</td>
<td>50·395</td>
<td>106·65</td>
</tr>
<tr>
<td>1907</td>
<td>Woernle</td>
<td>2</td>
<td>50·394</td>
<td>106·64</td>
</tr>
<tr>
<td>1908</td>
<td>Kemmerer</td>
<td>9</td>
<td>50·382</td>
<td>106·38</td>
</tr>
<tr>
<td>1892</td>
<td>Keller and Smith</td>
<td>9</td>
<td>50·508</td>
<td>107·13</td>
</tr>
<tr>
<td>1905</td>
<td>Amberg (i)</td>
<td>5</td>
<td>50·550</td>
<td>107·31</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>12</td>
<td>50·395</td>
<td>106·65</td>
</tr>
<tr>
<td>1907</td>
<td>Woernle</td>
<td>5</td>
<td>50·397</td>
<td>106·66</td>
</tr>
<tr>
<td>1905</td>
<td>Amberg (iii)</td>
<td>5</td>
<td>50·388</td>
<td>106·62</td>
</tr>
<tr>
<td>1912</td>
<td>Shinn</td>
<td>9</td>
<td>50·408</td>
<td>106·70</td>
</tr>
</tbody>
</table>

Two of the preceding investigators determined the chlorine in the compound by weighing it as silver chloride: first, Bailey and Lamb, who collected the ammonium chloride evolved when palladosamine chloride was heated in hydrogen; and, secondly, Amberg, who precipitated the chlorine in his filtrates after removing the palladium (electrolytically in series (i) and with hydrazine sulphate in series (iii) above):

\[
2\text{AgCl} : \text{Pd(NH}_3\text{)}_2\text{Cl}_2 : : 100-000 : x
\]

<table>
<thead>
<tr>
<th>Date</th>
<th>Experimenter</th>
<th>No. of Expts</th>
<th>Value of (x)</th>
<th>Atomic Weight of Palladium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1892</td>
<td>Bailey and Lamb</td>
<td>5</td>
<td>78·807</td>
<td>106·61</td>
</tr>
<tr>
<td>1905</td>
<td>Amberg (i)</td>
<td>4</td>
<td>78·818</td>
<td>106·64</td>
</tr>
<tr>
<td></td>
<td>(iii)</td>
<td>6</td>
<td>78·814</td>
<td>106·63</td>
</tr>
</tbody>
</table>

\(^1\) Kemmerer, \textit{J. Amer. Chem. Soc.}, 1908, 30, 1701.
\(^2\) Amberg, \textit{Annalen}, 1905, 341, 255.
Haas, Gebhardt, and Gutbier analyzed palladosammme bromide by reduction in hydrogen, with the following results:

\[
Pd(NH_3)_2Br_2 \cdot Pd : 100-000 : x
\]

<table>
<thead>
<tr>
<th>Date</th>
<th>Experimenter</th>
<th>No. of Expts.</th>
<th>Value of (x)</th>
<th>Atomic Weight of Palladium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1908</td>
<td>Haas</td>
<td>7</td>
<td>35.492</td>
<td>106.68</td>
</tr>
<tr>
<td>1909</td>
<td>Gebhardt</td>
<td>7</td>
<td>35.491</td>
<td>106.67</td>
</tr>
<tr>
<td>1909</td>
<td>Gutbier, Haas, and Gebhardt</td>
<td>4</td>
<td>35.495</td>
<td>106.69</td>
</tr>
</tbody>
</table>

A few investigations have been made with other palladium compounds. Joly and Leidié used potassium chlor-palladite, \(K_2PdCl_4\). The dried salt was electrolysed in a solution acidulated with hydrochloric acid, the deposit of palladium weighed, the potassium chloride recovered from the liquid by evaporation and also weighed. Three experiments were carried out with a salt containing a little water, and a second series of four experiments made with a salt that had been dried in vacuo at 100°C. The results were not very concordant. Finally, in two experiments the salt was reduced by heating it in hydrogen, and the palladium and potassium chloride determined in the residue:

1st series.—2KCl : Pd : 100-000 : 70-979 whence \(Pd = 105\cdot84\)

2nd series.—\(K_2PdCl_4\) : Pd : 100-000 : 32-450 "  \(Pd = 105\cdot70\)

\(K_2PdCl_4\) : 2KCl : 100-000 : 45-528 "  \(Pd = 107\cdot50\)

2KCl : Pd : 100-000 : 71-257 "  \(Pd = 106\cdot26\)

3rd series.—\(K_2PdCl_4\) : Pd : 100-000 : 32-480 "  \(Pd = 105\cdot84\)

\(K_2PdCl_4\) : 2KCl : 100-000 : 45-700 "  \(Pd = 106\cdot26\)

2KCl : Pd : 100-000 : 71-055 "  \(Pd = 105\cdot95\)

Hardin employed three compounds, diphenylpalladodi ammonium chloride and bromide, and palladium ammonium bromide. Each compound was analysed for palladium by reduction at a red heat in hydrogen, with the following results:

7 expts. \(Pd(C_6H_5-NH_2Cl)_2\) : Pd : 100-000 : 29-390 whence \(Pd = 107\cdot00\)

5 "  \(Pd(C_6H_5-NH_2Br)_2\) : Pd : 100-000 : 23-622 "  \(Pd = 107\cdot01\)

4 "  \((NH_4)_2PbBr_4\) : Pd : 100-000 : 28-1185 "  \(Pd = 106\cdot94\)

Kemmerer, in addition to studying palladosammine chloride, reduced the corresponding cyanide to the metal in a stream of hydrogen:

6 expts. \(Pd(NH_3)_2(CN)_2\) : Pd : 1000-000 : 55-291 whence \(Pd = 106\cdot46\)

There is a wide variation in the preceding results, which point strongly, however, to a value for the atomic weight of palladium about


4 Kemmerer, *loc. cit.*
half-way between \( Pd = 106 \) and \( Pd = 107 \). Shinn\(^1\) expresses the opinion that palladosammine chloride, which has been used in most of the determinations, has probably never been prepared perfectly free from traces of palladium ammonium chloride, in which case most workers have not analysed a truly homogeneous substance. Should this criticism be substantiated, it is probable that a similar one would hold against the corresponding bromide and cyanide and the organic derivatives employed by Hardin.

The International Committee's table for 1918 gives

\[ Pd = 106.7. \]

This value is probably not far from the truth, since with the exception of Kemmerer's results and the undoubtedly defective series (i) of Amberg's electrolytic determinations, all the modern values for the atomic weight of palladium fall between the limits 106.6 and 106.7.

**ALLOYS OF PALLADIUM**

Palladium yields a few alloys, the most important of which are those containing gold.

With copper the freezing-point curve falls steadily from the freezing-point of palladium to that of copper, the portion representing alloys rich in copper being nearly horizontal. There is no evidence of the formation of compounds, the two metals yielding complete series of mixed crystals. The alloys are harder than the individual metals, exhibiting a maximum hardness with equal parts of each by weight.\(^2\)

With gold, palladium likewise yields no compounds, the freezing-point curve falling continuously, and lying concave to the axis of concentration. The hardness of the alloys increases up to 70 per cent. of palladium and then decreases. Alloys containing more than 10 per cent. of palladium are white.\(^3\)

A couple consisting of gold wire and a wire containing 60 per cent. of gold, the remainder being palladium, has approximately six times the thermo-electromotive force of a platinum-rhodium couple. Its utility, however, is curtailed by the liability to undergo disintegration which characterises palladium alloys.\(^4\)

The addition of gold to palladium first increases and then reduces the power of the latter metal to occlude hydrogen, the reduction being proportional to the amount of gold in the alloy. The occlusion is reduced to nil in the presence of 75 per cent. of gold.\(^5\)

Alloys of palladium and gold, containing from 60 to 90 per cent. of the latter metal, are known as *rhotanium*, and, on account of their high melting-point, strength, and incorrodibility, have been recommended as substitutes for platinum.

An alloy of palladium and gold has been placed on the market under the name of *Palan* as a platinum substitute.\(^6\) It is claimed to be even

---

\(^1\) Shinn, *loc. cit.*


\(^3\) Ruer, *ibid.*, p. 391.


superior to platinum in certain respects. It melts at 1370° C., and has a density of 17.22. When heated strongly it loses only very slightly in weight, being superior in this respect to platinum containing 2-4 per cent. of iridium, although inferior to that containing only 0.6 per cent. of iridium. Its comparative freedom from iron is an advantage, and in its resistance to hydrochloric, nitric, hydrofluoric, and sulphuric acids, and to sodium hydroxide solution, and fused sodium carbonate compares favourably with that of platinum. It is not so good, however, for potassium pyrosulphate fusions.

The freezing-point curve of mixtures of palladium and silver is similar to that of palladium and gold, and no compounds appear to be formed. The hardness of the alloys lies between that of the components.

An alloy containing 5 parts by weight of palladium and 4 of silver was found by Graham to be still capable of absorbing hydrogen.

Palladium silver alloys admit of receiving a high polish, and retain their bright surface. An alloy containing 38 per cent. of palladium, the remainder being silver, was formerly used for dental purposes.

With lead the freezing-point curve exhibits two maxima, namely, at 454° C. and 1219° C., corresponding to the compositions PdPb₂ and Pd₃Pb, respectively. Three breaks occur at 495°, 596°, and 830° C. respectively. The first and last, namely, at 495° and at 830° C., indicate the existence of the compounds PdPb and Pd₃Pb, and which decompose below their melting-points. It is not yet certain what the composition of the alloy represented by the break at 596° C. may be.

Interesting support to the belief that the compound Pd₃Pb can exist is afforded by the results of experiments to determine the difference of potential between various alloys and pure lead in a normal solution of lead nitrate. The alloys were prepared by melting the palladium and lead under a mixture of lithium chloride and either potassium or barium chloride. Alloys containing less than 38 per cent. of palladium have a potential practically identical with that of pure lead, whilst those containing more than this amount of palladium exhibit a higher potential, which at first rapidly increases with the palladium. Between 20 and 90 per cent. of palladium the alloys are harder than the individual components, a maximum occurring with 65 per cent. of palladium.

Palladium and nickel yield a continuous series of solid solutions. The equilibrium diagram exhibits a flat minimum near 1208° C., that is, between 40 and 60 per cent. of palladium. The alloys are all more readily susceptible to attack by concentrated nitric acid than are the individual metals themselves. Alloys up to 87 per cent. of palladium are magnetic, but the magnetic power rapidly declines from 40 per cent. of palladium upwards. The alloys can be forged to a certain extent, those containing a high percentage of nickel being somewhat more easily worked.

3 Graham, Phil. Trans., 1868, 156, 399.
Palladium Amalgam is readily prepared by triturating finely divided palladium with mercury. Union takes place with evolution of heat and sometimes accompanied by explosion.

The finely divided metal is obtained for this purpose by reduction of palladous chloride with strips of metallic zinc, the palladium deposit being carefully washed and dried. After prolonged exposure to air it appears to lose its affinity for mercury, possibly on account of slow oxidation.

Palladium amalgam is sometimes used as a filling for teeth.

The following table, giving references to the more important researches on alloys of palladium, may prove useful to the reader:

<table>
<thead>
<tr>
<th>Elements alloying with Palladium</th>
<th>Remarks</th>
<th>Authority</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td></td>
<td>Debray, <em>Compt. rend.</em> 1856, 43, 925.</td>
</tr>
<tr>
<td>Antimony</td>
<td>Existence indicated of Pd₃Sb, Pd₂Sb₂, PdSb, and PdSb₂.</td>
<td>See p. 206.</td>
</tr>
<tr>
<td>Copper</td>
<td>No compound. Complete series of mixed crystals.</td>
<td>See p. 192.</td>
</tr>
<tr>
<td>Gold</td>
<td>No compound. Alloys used commercially.</td>
<td>See p. 192.</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td>Deville and Debray, loc. cit.</td>
</tr>
</tbody>
</table>

**COMPOUNDS OF PALLADIUM**

Three classes of palladium salts are known, namely, palladous salts, in which the metal functions as a divalent atom, and palladic salts, in which the metal is trivalent and tetravalent. The palladous salts are stable, but upon ignition yield metallic palladium.

Palladic salts are less well known in the free state, being highly unstable, although, combined with other salts, they yield stable compounds. Examples of these are the chlor-palladates, of general formulæ
M₂PdCl₅ and M₂PdCl₆. The latter correspond to the chlor-platinates, with which indeed they are isomorphous but possess less stability.

Palladous salts are readily oxidised to palladic compounds, particularly when warmed. For example, a solution of palladous nitrate warmed with concentrated persulphate solution is oxidised to a brown, palladic compound, which decomposes hydrogen peroxide and ammonia vigorously, gaseous products being evolved. With hydrochloric acid it yields free chlorine.

When a solution of potassium chlor-palladite or brom-palladite is warmed with a persulphate in the presence of the corresponding halogen acid the halogen palladate is precipitated on cooling. This reaction is interesting as affording a method of separating palladium from certain other metals.¹

Palladous salts possess catalytic properties. For example, they accelerate the oxidation of oxalic acid by persulphates and, to a less extent, by nitric acid. This is explained on the assumption that the palladous salt is alternately oxidised to a palladic derivative by the oxidising agent and reduced by the oxalic acid.

Ammonia is likewise oxidised by persulphates in the presence of a palladous salt.

Palladium resembles both nickel and cobalt in yielding double nitrites and cyanides.

Palladium salts are reduced to metallic palladium by hydrazine, whether in acid or alkaline solution, and the product is entirely soluble in aqua regia.²

PALLADIUM AND FLUORINE

Palladous Fluoride, PdF₂, is obtained as a dark-coloured, crystalline salt by heating palladium to dull redness in fluorine.³ When the temperature is raised to bright redness the salt decomposes, leaving metallic palladium.

PALLADIUM AND CHLORINE

Palladous Chloride, Palladium Dichloride, PdCl₂, is obtained in the anhydrous condition as a sublimate on heating spongy palladium to dull redness in dry chlorine.⁴ The monosulphide, PdS, when heated in chlorine is converted into the anhydrous chloride, and the same salt is produced by dehydrating the dihydrate, PdCl₂.2H₂O, at a slightly elevated temperature.

Palladium chloride can be distilled at a low red heat in a current of chlorine. It then yields a sublimate of dark red, needle-shaped crystals⁴ which deliquesce in the air.

When heated in air to 160° C. chlorine is evolved, and even at 100° C., after prolonged heating, traces of chlorine are driven off. When heated in an inert gas such as carbon dioxide, chlorine is evolved at 250° C. It is reduced by hydrogen in the cold.⁵

¹ Scaglarini and Berti-Ceroni, Gazzetta, 1916, 46, ii, 51.
² Paal and Amberger, Ber., 1905, 38, 1388. Compare Jannasch and Rostosky, Ber., 1904, 37, 2441; Jannasch and Bettges, Ber., 1904, 37, 2210.
When palladium dichloride is dissolved in water, and ammonia added in sufficient excess to dissolve the flesh-coloured precipitate, the *diammoniate*, PdCl₂·2NH₃, may be obtained as a precipitate by diluting with a large volume of water and acidulating with hydrochloric acid. It may be dried at 110° to 120° C., and has been used for the determination of the atomic weight of palladium (see p. 189). Density 2·5.

The *dihydrate*, PdCl₂·2H₂O, is obtained by crystallisation from the solution obtained by dissolving palladium in hydrochloric acid containing free chlorine, or in aqua regia. In the latter case the solution is first evaporated with hydrochloric acid in order to expel all the nitrogen products.

The salt crystallises as a brown, hygroscopic mass, which undergoes decomposition in excess of water, yielding a precipitate which possibly contains an oxychloride. Carbon monoxide ¹ passed into a solution of palladium dichloride effects its decolourisation, precipitating the metal as a black powder. The dilute solution is also completely reduced by hydrogen in twenty-four hours at ordinary temperature.²

**Dichlor-palladous Acid, H₂PdCl₄(OH)₂.**—On adding a silver salt to a solution of palladous chloride a precipitate is obtained, not of silver chloride, but of a complex compound of composition PdCl₂·2AgOH or [PdCl₂(OH)₂]₂Ag₂. It seems possible, therefore, that palladous chloride can, in aqueous solution, act like an acid, yielding the ions:

\[
PdCl₂\text{OH}^- + 2H^+.
\]

In addition to the silver salt, the lead and thallium derivatives, [PdCl₂(OH)₂]Pb·Pb(OH)₂ and [PdCl₂(OH)₂]Tl₂ respectively, have also been obtained.

All three salts are hydrolysed by hot water, the silver salt being the least sensitive.³

**Tetrachlor-palladites, M₂PdCl₄**

Palladium dichloride combines with chlorides of certain other metals to yield *chlor-palladites*, of general formula M₂PdCl₄. These are analogous to the chlor-platinites, M₂PtCl₄, the potassium salts of the two series being isomorphous.

**Potassium Chlor-palladite, K₂PdCl₄**, the most important salt of this series, is readily obtained by concentrating a solution of palladous chloride with excess of potassium chloride.⁴

Insoluble in absolute alcohol, the crystals readily dissolve in water, yielding a reddish brown solution. Heated to 100° C. they still retain some water, and begin to decompose at 105° C., a fact which renders it difficult to obtain the crystals in a perfectly dry condition. At red heat, potassium chloride and metallic palladium are formed.

When boiled with excess of water potassium chlor-palladate, K₂PdCl₆, is formed. The boiling solution is reduced by alcohol and by sulphur dioxide. With ammonia, an ammoniate is produced.

---

³ Bellucci and Cesaris, Gazzetta, 1908, 83, ii, 602.
Ammonium Chlor-palladite, (NH_4)_2PdCl_4, is obtained in an analogous manner to the potassium salt, and is interesting since it yields, upon heating in hydrogen, a residue of spongy palladium in a condition particularly suitable for catalytic activity.

The salt yields dark green prisms, soluble in water but insoluble in absolute alcohol.

Cesium Chlor-palladite, Cs_2PdCl_4, is precipitated on mixing concentrated solutions of cesium chloride and palladous chloride as a light brown deposit, which upon recrystallisation from hot water yields needles of the same colour.

Rubidium Chlor-palladite, Rb_2PdCl_4, prepared in an analogous manner to the preceding salt, crystallises from hot water in light brown silk-like needles.

The chlor-palladites of the following metals have also been prepared: sodium, Na_2PdCl_4; calcium, CaPdCl_4; barium, BaPdCl_4; glucinium, GlPdCl_4·6H_2O; magnesium, MgPdCl_4; zinc, ZnPdCl_4; cadmium, CdPdCl_4; aluminium, AlPdCl_5·10H_2O; nickel, NiPdCl_4; manganese, MnPdCl_4.

Palladium Trichloride, PdCl_3, is obtained in unstable solution by dissolving the brown hydrated sesquioxide in hydrochloric acid.

Palladium trichloride is also formed during the action of chlorine upon the dichloride. It is not formed during the reduction of the hexachlor-palladates, M_2PdCl_6.

Pentachlor-palladates, M_2PdCl_5

When the sesquioxide, Pd_2O_3·aH_2O, is suspended in ether in the presence of rubidium chloride at the temperature of ether and solid carbon dioxide, small greyish green crystals of the double salt, Rubidium Pentachlor-palladate, 2RbCl·PdCl_5 or Rb_2PdCl_5, are obtained. Cesium yields an analogous salt, Cs_2PdCl_5, in the form of dark green crystals.

Both salts decompose in contact with water, the corresponding tetrachlor-palladites, Rb_2PdCl_4 and Cs_2PdCl_4 respectively, being obtained.

Potassium chloride, in similar circumstances, does not yield a pentachlor-palladate, but only the tetrachlor-palladide, K_2PdCl_4, and the double salt, PdCl_3·4KCl.

Hexachlor-palladates, M_2PdCl_6

Although palladium tetrachloride, PdCl_4, analogous to platinic chloride, PtCl_4, is not known in the free state, salts known as chlor-palladates, M_2PdCl_6, corresponding to, and isomorphous with, the chlor-platinates, M_2PtCl_6, have been prepared. They are much less stable than the platinum derivatives, but the fact that they can exist at all, when nickel yields no such compounds, affords an interesting link between palladium and platinum, and further justifies the inter-
mediate position of palladium between nickel and platinum in the third vertical column in Group VIII of the Periodic Table.

Potassium Chlor-palladate, $K_2\text{PdCl}_6$.—This is the most important salt of the series, and is conveniently obtained by passing chlorine through an aqueous, saturated solution of potassium chlor-palladite. The same salt is produced on dissolving palladium in aqua regia or in water saturated with hydrogen chloride and chlorine, and adding a saturated solution of potassium chloride. The liquid is evaporated to dryness, the residue washed with potassium chloride solution and finally with ice-water. Scaglierini and Berti-Ceroni prepared it by warming the chlor-palladite with potassium persulphate in the presence of hydrochloric acid. The salt precipitates out on cooling.

The crystals obtained in this way are red in colour, and isomorphous with the corresponding chlor-platinate. Density 2.788. On heating they turn black, but regain their red colour on cooling. They are readily reduced on warming in a current of hydrogen gas, whilst ignition converts them first into the chlor-palladite and finally into potassium chloride and metallic palladium.

Potassium chlor-palladate dissolves in water, but is only slightly soluble in ice-water, and is insoluble both in saturated potassium chloride solution and in alcohol. The aqueous solution undergoes partial dissociation, and on boiling with excess of water, potassium chlor-palladate is formed. Aqueous hydrochloric acid dissolves the salt without decomposition, whilst ammonia converts it into an ammoniate.

Cesium Chlor-palladate, $\text{Cs}_2\text{PdCl}_6$, may be obtained in an analogous manner to the potassium salt, namely, by chlorinating an aqueous solution of cesium chlor-palladite. A brownish yellow crystalline precipitate results, which is very stable and almost insoluble in cold water. On boiling with water chlorine is evolved; it attacks ammonia, evolving nitrogen; concentrated sulphuric acid when warmed with the salt causes an evolution of chlorine and hydrogen chloride.

Rubidium Chlor-palladate, $\text{Rb}_2\text{PdCl}_6$.—This salt is obtained as a yellowish red precipitate in a similar manner to the preceding salt. Insoluble in cold water, it is decomposed by boiling water, and in its other properties closely resembles the cesium analogue.

The chlor-palladates of the following metals have been described: ammonium, $\text{(NH}_4\text{)}_2\text{PdCl}_6$; gluconium, $\text{GlPdCl}_6\cdot8\text{H}_2\text{O}$; magnesium, $\text{MgPdCl}_6\cdot6\text{H}_2\text{O}$; zinc, $\text{ZnPdCl}_6\cdot6\text{H}_2\text{O}$; nickel, $\text{NiPdCl}_6\cdot6\text{H}_2\text{O}$; manganese, $\text{MnPdCl}_6\cdot6\text{H}_2\text{O}$.

PALLADIUM AND BROMINE

Palladous Bromide, PdBr$_2$, is produced in small quantity by the action of bromine water upon palladium. It is more easily obtained in bulk by the action of a mixture of hydrobromic and nitric acids upon the metal. The nitrous acid is removed by boiling with excess of hydrobromic acid. Upon evaporation the salt is obtained as a reddish
brown mass, insoluble in water, but soluble in aqueous hydrobromic acid \(^1\) and in alcohol. Ammonia converts it into the diammoniate, 
\[
palladosammine dibromide, \text{PdBr}_2.2\text{NH}_3.
\]

**Brom-palladites, \(\text{M}_2\text{PdBr}_4\)**

With bromides of the alkali metals palladous bromide yields pallado-
bromides or brom-palladites, of general formula \(\text{M}_2\text{PdBr}_4\), analogous to the chlor-palladites already considered.

**Potassium Brom-palladite,** \(\text{K}_2\text{PdBr}_4\), is obtained \(^1\) by dissolving equivalent weights of the bromides of potassium and palladium in water containing hydrobromic acid. Upon evaporation the anhydrous salt crystallises in reddish brown needles, which are very stable.

Digestion of the aqueous solution of this salt with bromine at a temperature not exceeding 70° C. yields the dihydrate, \(\text{K}_2\text{PdBr}_4.2\text{H}_2\text{O}\), which separates out in long, dark brown, shining needles. These upon exposure to air rapidly lose their lustre and acquire the reddish brown colour of the anhydrous salt. Owing to the rapidity with which they lose their combined water, complete analysis of the crystals is difficult.

**Ammonium Brom-palladite,** \((\text{NH}_4)_2\text{PdBr}_4\), may be prepared \(^1\) in a similar manner to the preceding salt. Its crystals are olive brown in colour, anhydrous, and very stable in air. They readily dissolve in water. Upon ignition a residue of palladium sponge is obtained.

**Caesium Brom-palladite,** \(\text{Cs}_2\text{PdBr}_4\), is precipitated as a dark brown mass on mixing concentrated solutions of caesium bromide and palladous bromide.\(^2\) Upon recrystallisation from dilute hydrogen bromide solution, fine reddish brown needles are obtained, which are anhydrous, and very soluble in water.

**Rubidium Brom-palladite,** \(\text{Rb}_2\text{PdBr}_4\), is obtained in a precisely similar manner to the caesium salt.\(^2\) It yields similar needle-shaped crystals, which are also reddish brown in colour.

**Sodium Brom-palladite,** \(2\text{Na}_2\text{PdBr}_4.2\text{H}_2\text{O}\), has been obtained \(^1\) by concentrating mixed solutions of the bromides of sodium and palladium over sulphuric acid in an evacuated desiccator. It separates out in large, deep red plates which are exceedingly deliquescent.

Brom-palladites of Barium,\(^3\) BaPdBr\(_4\); Strontium,\(^3\) SrPdBr\(_4\); Manganese,\(^1\) and Zinc,\(^2\) have also been described.

**Brom-palladates, \(\text{M}_2\text{PdBr}_6\)**

Although palladium tetrabromide is not known, compounds of the type \(\text{M}_2\text{PdBr}_6\), termed brom-palladates, have been prepared. Of these the most important is:

**Potassium Brom-palladate,** \(\text{K}_4\text{PdBr}_6\), which is precipitated from a solution of potassium brom-palladate on passing through it a current of bromine vapour.\(^2\) It also results on oxidising a solution of the brom-palladate with potassium persulphate in the presence of hydrobromic acid.\(^4\) It crystallises in beautiful black octahedra, which dissolve sparingly in water, yielding a reddish brown solution.

Boiling water and hot concentrated sulphuric acid each decompose

---

the salt, bromine being evolved. Ammonia is immediately decomposed by it, with evolution of nitrogen.

**Ammonium Brom-palladate**, \((\text{NH}_4)_2\text{PdBr}_6\), is obtained in a similar manner to the preceding salt, ice-cold solutions being employed.\(^1\) The salt crystallises in black, regular octahedra, which are stable in air and sparingly soluble in cold water, yielding a reddish brown solution. Upon heating in a dry tube, bromine vapour is at first evolved, ammonium bromide next sublimes, and a residue of palladium sponge remains behind. Towards hot water, sulphuric acid, and ammonia the salt behaves in an analogous manner to the preceding salt.

**Cesium Brom-palladate**, Cs\(_2\)PdBr\(_6\), and **Rubidium Brom-palladate**, Rb\(_2\)PdBr\(_6\), have also been prepared. They resemble the potassium salt in appearance and general properties.\(^4\)

**Palladium AND IODINE**

**Palladous Iodide**, PdI\(_2\)—Palladium is stained by iodine solution and tarnished by iodine vapour, whilst a certain amount of combination between the two elements takes place when they are heated together, if the metal is in a finely divided condition. Palladium is slowly attacked by a mixture of nitric and hydriodic acid. In each of these cases a little palladous iodide is produced.

A convenient method of preparing the salt consists in adding potassium iodide to a slight excess of palladous chloride solution,\(^3\) when it is precipitated as a black mass, readily soluble in excess of potassium iodide. When dried in air it contains one molecule of water; heated to 300–360°C it decomposes, evolving iodine. In order to remove the last traces of iodine, however, it is necessary to heat to redness in a current of hydrogen.

Ammonia converts palladous iodide into the diammoniate, PdI\(_2\).2NH\(_3\). Although insoluble in water, alcohol, and ether, it dissolves slightly in hydriodic acid, and easily in aqueous potassium iodide, yielding:

**Potassium Iodopalladite**, K\(_2\)PdI\(_4\), which, upon concentration, crystallises out as black, hygroscopic cubes.\(^2\)

**Palladium AND OXYGEN**

The existence of five oxides of palladium has at various times been postulated, namely, the *suboxide*, Pd\(_2\)O; *penta palladium hexoxide*, Pd\(_5\)O\(_6\); the *monoxide*, PdO; the *dioxide*, PdO\(_2\), and the *sesquioxide*, Pd\(_3\)O\(_5\).

The *suboxide*, Pd\(_2\)O, was believed by Berzelius to be formed during the superficial oxidation of palladium and to cause the play of colours exhibited by the tarnish. Kane\(^3\) and Wilm\(^4\) both believed that they had obtained the suboxide, but in 1892 Wilm\(^5\) showed that, in his experiments, oxidation had not been carried to completion, otherwise

---

1 Gutbier and Krell, *Ber.*, 1905, 38, 2385.
2 Lassaigne, *J. Chim. méd.*, 1833, [i], 9, 447; 1835, [ii], 1, 57; 1838, [ii], 5, 349; 1851, [iii], 7, 142; Grampe, *Ber.*, 1874, 7, 1721.
3 Kane, *Phil. Trans.*, 1842, p. 276.
4 Wilm, *Ber.*, 1882, 15, 2225.
5 Wilm, *Ber.*, 1892, 25, 220.
the monoxide would have been formed. In view of this it seemed unlikely that the suboxide exists, and this is supported by Wöhler and König.1

Schneider 2 believed he had obtained the oxide, Pd₃O₆, by fusing the double palladium potassium sulphide with sodium hydroxide and potassium nitrate. It is very doubtful, however, if this is to be regarded as a separate chemical entity.3

**Palladous Oxide, PdO.—** Palladous oxide was obtained by Berzelius by strongly heating palladium amalgam, by precipitating palladous salt solutions with alkali, as well as by fusing metallic palladous with alkalis.4

Palladous oxide is also obtained in the anhydrous condition by heating palladous nitrate 5 to a high temperature, but the simplest and easiest method consists in hydrolysing a faintly acid solution of the nitrate by boiling with water.6

When palladium is heated to dull redness in oxygen palladous oxide is formed. But it is difficult to oxidise the metal completely by this method owing to the sintering of the metal, which renders oxidation slow. Palladium sponge is most suitable for the purpose, and should be heated in pure oxygen at temperatures rising slowly from 700° C. to 840° C.7

The colour of palladous oxide varies according to its method of preparation. Prepared by the action of alkali upon palladous salts in aqueous solution, it has a yellowish brown colour which becomes darker on prolonged boiling. The product obtained by the hydrolytic decomposition of the nitrate is almost black, and it may well be that the extent of hydration is responsible for these changes.

Air-dried specimens contain rather more water than corresponds to one molecule; when heated on the water-bath the residual water corresponds to about two-thirds of a molecule, but the last traces are not removed even at 500° C.6

The freshly precipitated oxide is readily soluble in dilute acids.

It is reduced by hydrogen in the cold, evolving so much heat that it becomes incandescent.

The dissociation of palladous oxide has been studied by Wöhler,8 who shows that it decomposes when heated, yielding palladium and oxygen, the reaction being reversible:

\[ \text{PdO } \rightleftharpoons \text{Pd } + \text{O.} \]

The dissociation pressure of palladium monoxide at 877° C. reaches 760 mm.

**Hydrated Palladium Sesquioxide, Pd₃O₅·2H₂O,** is conveniently prepared 9 by electrolytic oxidation of palladous nitrate. This is effected by cooling a concentrated solution to 8° C., and electrolysis with a current density of 0.5 amperes per sq. cm. It may also be obtained by ozonising a solution of palladous nitrate.

3 Wöhler and König, loc. cit.
The hydrated sesquioxide is thrown out as a brown precipitate which may be washed quite pure with ice-cold water. It is unstable, readily soluble in hydrochloric acid, yielding an unstable solution containing palladium trichloride.

**Hydrated Palladium Dioxide**, PdO₂·xH₂O. may be obtained, more or less contaminated with alkali, by decomposing a solution of potassium palladate with a slight excess of potassium hydroxide.¹

The brown precipitate is washed with hot water and dried over concentrated sulphuric acid. The product thus obtained has or.e or two molecules of combined water according to circumstances.

Mailfert ² prepared palladium dioxide free from alkali by the action of ozone in the cold on palladous chloride in dilute alkaline solution. The product, however, contained traces of basic salt. The reaction probably takes place according to the following equation:

\[ \text{Na}_2\text{PdCl}_4 + 2\text{NaOH} + \text{O}_3 + \text{H}_2\text{O} = 4\text{NaCl} + \text{O}_2 + \text{PdO}_2\cdot2\text{H}_2\text{O}. \]

Leidié and Quennessen ³ prepared the dioxide by treatment of palladium sponge with sodium peroxide, but unfortunately were unable to isolate it.

It is best prepared by electrolytic oxidation of palladous nitrate in acid solution. This is effected by cooling a concentrated solution to 8°C, and effecting electrolysis with a current density of 0.5 amperes/cm.² At first the sesquioxide, Pd₂O₃·xH₂O, is formed, but by continued electrolysis the dioxide is ultimately obtained.⁴ This, curiously enough, is not a result of direct oxidation, but one of decomposition followed by oxidation, the sesquioxide splitting up into the dioxide and monoxide, the latter dissolving in the free acid and undergoing oxidation again.

Palladium dioxide obtained by the method of Berzelius is a bright brown precipitate which gradually becomes dark brown in the cold but black on boiling with water or treatment with dilute acids. The water content varies considerably, but when dried over sulphuric acid to the point at which it becomes powdery it retains two molecules of water. Prolonged drying may reduce this to one molecule, which, however, is held very tenaciously.⁵ Palladium dioxide is not a very stable substance. When freshly prepared it is decomposed by boiling with water, yielding the monoxide. It is reduced by hydrogen at the ordinary temperature, evolving so much heat in the process that the mass becomes incandescent.

Hydrogen peroxide reduces it both in acid and in alkaline solution. It oxidises organic substances when boiled with their solutions.

Palladium dioxide cannot exist in air at temperatures above 200°C as it decomposes according to the equation:

\[ \text{PdO}_2 = \text{PdO} + \text{O}. \]

The reverse reaction takes place too slowly to be observed.⁶

---

PALLADIUM AND SULPHUR

Palladium Subsulphide, $\text{Pd}_2\text{S}$.—This sulphide has been prepared by heating to bright redness a mixture of palladous sulphide (1 part) with ammonium chloride (6 parts), sodium hydroxide (12 parts), and flowers of sulphur (12 parts). The product is washed with cold water.¹

Another method consists ² in igniting palladousammine chloride, $\text{PdCl}_2.2\text{NH}_3$, with 25 per cent. of its weight of sulphur in a crucible under a layer of borax, at the temperature at which gold melts \textit{(circa 1062° C.)}.

As obtained by these methods palladium subsulphide is a hard, grey, metallic-looking mass, with a granular fracture. It is amorphous; density 7·3; and it is soluble in aqua regia.

Palladous Sulphide, Palladium Monosulphide, $\text{PdS}$, results on heating together sulphur and ammonium chlor-palladate ³; it is also formed ⁴ by passing pure hydrogen sulphide over palladousammine chloride at 70° to 80° C. The mass becomes black, and at higher temperatures ammonium chloride volatilises, leaving a residue, insoluble in individual mineral acids, but soluble in mixtures such as aqua regia.

As obtained in either of the foregoing ways, palladous sulphide is a hard, metallic-looking substance, melting at approximately 950° C., and insoluble in all ordinary solvents.

On passing hydrogen sulphide through a solution of a palladous salt, a dark brown precipitate is obtained, which is presumably another form of palladous sulphide.⁵ It is insoluble in ammonium sulphide and in hydrochloric acid, but it dissolves both in nitric acid and in aqua regia. When heated in air, a basic sulphate is produced, whilst in chlorine palladous chloride is formed. Potassium cyanide gradually effects its solution. With sulphides of the alkali metals, sulpho- or thio-palladites, $\text{M}_2\text{Pd}_3\text{S}_4$, are formed.

Potassium Thio-palladite, $\text{K}_2\text{Pd}_3\text{S}_4$, is obtained ¹ as hexagonal needles on heating to redness a mixture of 1 part of palladous sulphide with 12 parts of a mixture containing caustic potash and sulphur in equal proportions. Extraction of the melt with water leaves a residue of crystalline thio-palladite. The crystals are insoluble in water, violet-blue in colour when moist, but metallic grey when dry. They dissolve, with decomposition, in hydrochloric acid.

The aqueous solution of potassium thio-palladite interacts with one of silver nitrate to yield insoluble hexagonal lamellæ of Silver Thio-palladite, $\text{Ag}_2\text{Pd}_3\text{S}_4$.

Palladic Sulphide, Palladium Disulphide, $\text{Pd}_2\text{S}_2$, has been prepared ¹ by igniting at bright red heat a mixture of ammonium chlor-palladate (1 part) with sulphur (12 parts) and sodium hydroxide (12 parts). The chlor-palladate may be replaced by palladous sulphide. The product is treated first with alcohol and then with dilute hydrochloric acid, when the disulphide is left as a dark brown crystalline powder, which readily dissolves in aqua regia. Exposure to air does not affect it, but

¹ Schneider, \textit{Pogg. Annalen}, 1870, 141, 519.
⁴ Smith and Keller, \textit{Ber.}, 1890, 23, 3378.
ignition in an inert gas causes the loss of sulphur. With sulphides of the alkali metals, double sulphides are formed, known generally as sulphi- or thio-palladates, and having the general formula \( \text{M}_2\text{PdS}_3 \).

**Potassium Thio-palladate**, \( \text{K}_2\text{PdS}_3 + \text{K}_2\text{S} \), is obtained mixed with palladium on reducing potassium thiopalladite in a current of hydrogen. Extraction with water leaves metallic palladium, whilst the solution contains potassium, palladium, and sulphur in proportions corresponding to the formula \( \text{K}_2\text{PdS}_3 \cdot \text{K}_2\text{S} \).

**Sodium Thio-palladate**, \( \text{Na}_2\text{PdS}_3 \).—On heating to redness a mixture containing equal parts of sodium hydroxide and sulphur with one-sixth of its weight of palladous sulphide or chloride and extracting the melt with water, sodium thio-palladate passes into solution, together with some sodium sulphide. Interaction with a solution of silver nitrate yields a brownish black crystalline powder consisting of **Silver Thio-palladate**, \( \text{Ag}_2\text{PdS}_3 \).

**Palladous Sulphite**, \( \text{Pd(SO}_4\text{)}_2 \), is not known.

**Sodium Pallado-sulphite**, \( \text{Na}_2\text{Pd(SO}_4\text{)}_2 \cdot 2\text{Na}_2\text{SO}_4 \), is obtained as a white precipitate on saturating a solution of palladous chloride with sulphur dioxide and subsequently neutralising with sodium carbonate.

**Ammonium Chlor-pallado-sulphite**, \( (\text{NH}_4)_2\text{PdCl}_2 \cdot \text{SO}_3 \cdot 2\text{H}_2\text{O} \), has been prepared.

**Palladous Sulphate**, \( \text{PdSO}_4 \cdot 2\text{H}_2\text{O} \).—This salt may be prepared in a variety of ways, notably by heating palladium with concentrated sulphuric acid, or a mixture of this with nitric acid; by heating palladous nitrate with sulphuric acid until all nitrous fumes have been expelled; by dissolving hydrated palladous oxide in sulphuric acid; and finally by fusing palladium and potassium hydrogen sulphate. The salt yields reddish brown crystals, which deliquesce in moist air. Soluble in water, they are decomposed in excess of that liquid, yielding a basic derivative, to which the formula \( \text{PdSO}_4 \cdot 7\text{PdO} \cdot 6\text{H}_2\text{O} \) has been given.

### PALLADIUM AND SELENIUM

Indications are not wanting that a *subseleneide*, of formula \( \text{Pd}_2\text{Se} \), may possibly be capable of existence.

**Palladous Selenide**, \( \text{PdSe}_2 \).—Berzelius found that palladium and selenium unite to form a refractory, grey selenide when heated together, their union being accompanied with evolution of heat.

Roessler obtained the selenide by igniting palladosammine chloride, \( \text{PdCl}_2 \cdot 2\text{NH}_3 \), with half its weight of selenium, using borax as a flux. The product has a metallic appearance, with a fine-grained fracture. It melts at a lower temperature than silver (960° C.) without loss of selenium even in air. It dissolves completely in aqua regia, and serves to illustrate the observation that selenides are usually more readily attacked by acids than the corresponding sulphides.

**Palladous Selenate**, \( \text{PdSeO}_4 \).—Palladium dissolves in selenic acid to a deep reddish brown solution which, on concentration, yields a mixture of palladous selenate and selenous acid. Pure palladous selenate, \( \text{PdSeO}_4 \), results when palladium is dissolved in a mixture of

---

selenous and nitric acids. It crystallises in dark brownish red, hygroscopic rhombs, and forms double salts with ammonium selenate or sulphate. When warmed with concentrated hydrochloric acid, chlorine is evolved.\(^1\)

**PALLADIUM AND NITROGEN**

**Palladous Nitrate**, \(\text{Pd(NO}_3\text{)}_2\), may be obtained by dissolving the metal in nitric acid of density 1.85 to 1.4, and cooling the concentrated solution, when the salt crystallises out in brownish yellow, orthorhombic crystals. These are deliquescent, and readily dissolve in water, yielding a solution that is not very stable. When heated, the crystals decompose, yielding palladous oxide.\(^2\)

Although **Palladous Nitrite** has not been isolated, double salts of general formula \(2\text{MNO}_2\cdot\text{Pd(NO}_2\text{)}_2\) or \(\text{M}_2\text{Pd(NO}_2\text{)}_4\) have been prepared. The most important of these is:

**Potassium Pallado-nitrite**, \(\text{K}_2\text{Pd(NO}_2\text{)}_4\), which is obtained by addition of potassium nitrite to a solution of palladous nitrate or chloride, and subsequent boiling.\(^3\) On crystallisation in the warm the anhydrous salt is obtained, whilst in the cold the **dihydrate**, \(\text{K}_2\text{Pd(NO}_2\text{)}_4\cdot2\text{H}_2\text{O}\), separates out as yellow, efflorescent, triclinic prisms.\(^4\) These are readily soluble in water, but less so in an aqueous solution of potassium chloride. The solution does not behave like one of an ordinary palladous salt towards chemical reagents. For example, it is not precipitated by hydrogen sulphide, nor even by mercuric cyanide, until after prolonged boiling, a fact that indicates its complex nature. It is not a simple double nitrite, but a pallado-nitrite in which the palladium occurs, not in the positive, but in the negative radicle.

**Potassium Chlor-pallado-nitrite**,\(^5\) \(\text{K}_3\text{PdCl}_3\text{(NO}_2\text{)}_2\);  
**Potassium Brom-pallado-nitrite**,\(^6\) \(\text{K}_3\text{PdBr}_3\text{(NO}_2\text{)}_2\); and  
**Potassium Iodo-pallado-nitrite**,\(^7\) \(\text{K}_5\text{PdI}_3\text{(NO}_2\text{)}_2\) have been prepared.  
**Silver Pallado-nitrite**,\(^8\) \(\text{Ag}_2\text{Pd(NO}_2\text{)}_4\), has been described.

**PALLADIUM AND PHOSPHORUS**

Palladium combines with phosphorus at high temperatures, but definite phosphides do not appear as yet to have been isolated. Similarly, hydrogen phosphide causes the precipitation of a mass, containing both palladium and phosphorus, when passed into an aqueous solution of a palladous salt. Complex chlorophosphides have been prepared.\(^9\)

**Palladium Dibromide Phosphorus Tribromide**, \(\text{PdBr}_3\cdot\text{PBr}_3\), is described as forming reddish brown, deliquescent crystals.\(^10\)

COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

PALLADIUM AND ANTIMONY

Palladium readily alloys with antimony, and the existence of the following compounds has been indicated, Pd₅Sb, Pd₅Sb₃, PdSb, and PdSb₂. The alloys have no magnetic power, and those containing up to about 85 per cent. of palladium are characterised by their brittleness.¹ The compound, Pd₅Sb, exhibits the maximum brittleness.

PALLADIUM AND CARBON

Palladium and carbon do not appear to unite to form a definite carbide, although when the two elements are heated together in the electric furnace palladium absorbs a certain amount of carbon, which, on solidification of the metal during cooling, is given up again as graphite.² Palladium Cyanide, Pd(CN)₂, was known to Berzelius;³ who obtained it by decomposition of a palladium salt with mercuric cyanide. It also results when palladium oxide is boiled with a solution of mercuric cyanide. These reactions afford a useful method of separating palladium from its congeners. When heated in air cyanogen is evolved and spongy palladium left.

Palladium cyanide is very stable; insoluble in acids, it dissolves in potassium cyanide, yielding:

Potassium Palladocyanide, K₂Pd(CN)₄·8H₂O, which crystallises on evaporation of the solution. Soluble in water and alcohol, it effloresces in air, and at 100° C. loses two molecules of water, yielding the monohydrate, K₂Pd(CN)₄·H₂O. At 200° C. it becomes anhydrous. It is isomorphous with the corresponding platino-cyanide.

Ammonium Palladocyanide is not known, palladosammines being obtained instead.

Sodium Palladocyanide, Na₂Pd(CN)₄·8H₂O, is prepared in an analogous manner to the potassium salt. It also yields a monohydrate, Na₂Pd(CN)₄·H₂O.

Pallado-cyanides of barium, BaPd(CN)₄·4H₂O; calcium, CaPd(CN)₄·4H₂O; and magnesium, MgPd(CN)₄·4H₂O, have also been prepared.⁴ Palladium Thiocyanate, Pd(CNS)₂, results as a brick-red precipitate on adding the requisite quantity of potassium thiocyanate to a solution of potassium chlor-palladite. It is soluble in excess of the thiocyanate,⁵ yielding Potassium Pallado-thiocyanate, K₂Pd(CNS)₉, which crystallises out in red needles upon evaporation.

PALLADIUM AND SILICON

On heating an intimate mixture of palladium and crystallised silicon to about 500° to 600° C. combination ensues with incandescence and fusion. The melting-point falls from 1587° C. (m.p. of Pd) to a

¹ Sander, Zeitsch. anorg. Chem., 1912, 75, 97; Roessler, ibid., 1895, 9, 55.
² Moissan, Compt. rend., 1896, 123, 16.
³ Berzelius, Pogg. Annalen, 1828, 13, 461. See also FeHling, Annalen, 1841, 39, 110; Rammelsberg, ibid., 1838, 28, 216; Pogg. Annalen, 1837, 42, 137; Wollaston, Ann. Chem. Phys., 1829, 47, 413.
⁴ H. Rössler, Zeitsch. Chem., 1866, 9, 175.
minimum of 670° C. upon addition of silicon, the minimum correspond-
ing to 6 per cent. Si. It then rises to 1400° C. with further addition of silicon up to 11.76 per cent. and corresponding to the composition Pd$_2$Si. The melting-point again falls to a minimum of 750° C. with 16 per cent. silicon, and rises to a maximum of 990° C. with 21 per cent. Si, corresponding to PdSi. This is followed by a third minimum of 825° C., after which the melting-point rises to that of pure silicon, namely, 1434° C.

**Palladium Monosilicide**, PdSi, is obtained as brilliant bluish grey fragments on treating any Pd-Si alloy, containing above 60 per cent. of silicon, with dilute potash. The free silicon dissolves, leaving the silicide as residue. Density 7.31 at 15° C.

It is attacked when heated in chlorine or fluorine. In air it tarnishes at dull red heat. Cold nitric acid and aqua regia attack it; caustic alkalies slowly act upon it; whilst hydrochloric and sulphuric acids are without action.¹

**Palladium Subsilicide**, Pd$_2$Si, has not been satisfactorily isolated.

**Detection and Estimation of Palladium.**—See Chapter X.

¹ Lebeau and Jolibois, *Compt. rend.*, 1908, 146, 1028.
CHAPTER VII

OSMIUM AND ITS COMPOUNDS

OSMIUM

Symbol, Os. Atomic weight, 190-9 (O = 16)

Occurrence and History.—Osmium occurs in nature alloyed with iridium as *iridosmine* or *osmiridium*, which is found as irregular flattened grains and, more rarely, as hexagonal prisms. It has a metallic lustre, tin-white to light steel-grey in appearance; hardness 6–7; density 19.8 to 21.12. It occurs in Choco, South America; in the Urals; in auriferous and other drifts in New South Wales; in auriferous beach-sands of North California; and also in gold washings of certain Canadian rivers.

The following analyses of osmiridium are typical:

<table>
<thead>
<tr>
<th>Source</th>
<th>Ir</th>
<th>Rh</th>
<th>Pt</th>
<th>Ru</th>
<th>Os</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. Grenada</td>
<td>70.40</td>
<td>12.80</td>
<td>0.10</td>
<td>—</td>
<td>17.20</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>57.80</td>
<td>0.63</td>
<td>—</td>
<td>6.37</td>
<td>35.10</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>California</td>
<td>53.50</td>
<td>2.60</td>
<td>—</td>
<td>0.50</td>
<td>43.40</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Australia</td>
<td>58.19</td>
<td>3.04</td>
<td>—</td>
<td>5.22</td>
<td>38.46</td>
<td>0.15</td>
<td>—</td>
</tr>
<tr>
<td>Borneo</td>
<td>58.27</td>
<td>2.64</td>
<td>0.15</td>
<td>—</td>
<td>38.94</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Urals</td>
<td>77.20</td>
<td>0.50</td>
<td>1.10</td>
<td>0.20</td>
<td>21.00</td>
<td>trace</td>
<td>—</td>
</tr>
</tbody>
</table>

Osmium was first identified as a new metal by Tennant, who derived its name from the Greek *σμη*, a smell, on account of the odour of its volatile tetroxide. He at first proposed to call it *ptene*, from *πτρεγος*, volatile or winged, but fortunately this name was not adopted.

Preparation.—Osmium may be isolated in a fairly pure state from the distillate, rich in that metal, obtained during the process of extracting ruthenium from osmiridium (see p. 186). The distillate is redistilled and collected in aqueous ammonia. Saturation with hydrogen sulphide yields a precipitate of the brown tetrasulphide, OsS₄, which is separated by filtration and heated in a closed carbon crucible to a high temperature, when the osmium is found on the upper part of the crucible as a brilliant metal, bluish in colour, somewhat resembling zinc.

Osmium may also be obtained in an amorphous, but pure, condition by reduction of the vaporised tetroxide, OsO₄, by passage through a red-hot porcelain tube together with a mixture of the

3 Tennant, *Phil. Trans.*, 1804, p. 411.
4 According to Deville and Debray, to the melting-point of nickel (1452°C.) or rhodium (1907°C.).
dioxide and monoxide of carbon.\textsuperscript{1} The osmium separates out as a powder.

Other methods consist in reducing aqueous solutions of osmium tetroxide with an alkali formate,\textsuperscript{2} when the metal is precipitated as a blue powder; by decomposing acidulated solutions of the tetroxide with zinc \textsuperscript{5} or with mercury,\textsuperscript{4} in which latter case the resulting amalgam is distilled.

Osmium may be obtained in a crystalline form by heating to redness with seven or eight times its weight of tin in a carbon crucible and allowing to cool slowly. The osmium separates on solidification and may be isolated by treatment with hydrochloric acid, which dissolves away the tin.\textsuperscript{5}

\textbf{Recovery of Osmium from Residues.}—Osmium residues containing organic matter do not yield up the whole of their osmium content as chloride when mixed with sodium chloride and ignited in chlorine.\textsuperscript{8} To recover the metal from such sources, therefore, it is convenient to ignite the mass in a current of oxygen, whereby the organic matter is oxidised to carbon dioxide, and the osmium to tetroxide, which is absorbed in alkaline reducing agents. As examples of the last named, alcohol in dilute caustic alkali solution, and alcoholic hydrazine hydrate, may be mentioned. The reduced solution is evaporated to dryness, and the residue ignited in hydrogen and cooled in carbon dioxide.

\textbf{Physical Properties.}—Osmium crystallises in cubes or obtuse rhombohedra of density ranging from 21.8 to 24.\textsuperscript{5} It is thus the most dense substance known. It is also very hard (hardness 7.5) and brittle, readily scratching, and in the massive form can be heated to the melting-point of zinc (419° C.) without volatilisation.\textsuperscript{5} At higher temperatures combustion takes place.

Osmium melts at 2200° to 2600° C., and may be distilled slowly in the electric furnace.\textsuperscript{7} At these high temperatures osmium can dissolve carbon. The specific heat of osmium is 0.03115.\textsuperscript{8}

The most intense lines in the spectrum are as follow\textsuperscript{9} :

\begin{itemize}
  \item \textbf{Arc} : 3752-69, 3782-34, 3794-08, 3963-80, 3977-39, 4112-19, 4185-96, 4178-40, 4212-06, 4261-01, 4420-64.
  \item \textbf{Spark} : 2909-19, 3772-71, 4135-95, 4261-01, 4420-62.
\end{itemize}

\textbf{Chemical Properties.}—Osmium oxidises when heated in air. The oxidation of the powdered metal begins at temperatures below 212° C. in air, and below 170° C. in oxygen,\textsuperscript{10} volatile vapours of the tetroxide, OsO\textsubscript{4}, being evolved. These vapours are intensely poisonous, producing temporary blindness and other unpleasant symptoms.\textsuperscript{5} Osmium is also oxidised when heated in steam. It is readily dissolved by

\begin{thebibliography}{9}
  \bibitem{1} Deville and Debray, \textit{Compt. rend.}, 1876, 82, 1076.
  \bibitem{2} Doebereiner, \textit{Annalen}, 1835, 14, 17.
  \bibitem{3} Vauquelin, \textit{Annales Chim.}, 1814, 89, 150.
  \bibitem{5} Deville and Debray, \textit{Ann. Chim. Phys.}, 1859, 56, 385.
  \bibitem{6} Gutbier, \textit{Chem. Zeit.}, 1913, 37, 857.
  \bibitem{7} Moissan, \textit{Compt. rend.}, 1906, 142, 189. See also Joly and \textit{Vèzes, ibid.}, 1893, 116, 577.
  \bibitem{8} Regnault, \textit{Ann. Chim. Phys.}, 1858, 46, 262; 1861, 63, 14.
  \bibitem{9} Exner and Haschek, \textit{Die Spektren der Elemente bei normalem Druck} (Leipzig and Wien, 1911).
  \bibitem{10} Šulo, \textit{Zeitsch. anorg. Chem.}, 1899, 19, 332.
\end{thebibliography}
COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

fuming nitric acid, and by aqua regia unless the osmium has previously been strongly heated.

Fluorine is without action in the cold, but upon warming combination takes place. Chlorine attacks osmium at high temperatures, the tetrachloride, OsCl₄, resulting at 650° to 700° C. Bromine vapour, however, is without action upon the metal.¹

When fused with a mixture of peroxide and nitrate of barium or sodium, osmium is dissolved.

**Osmium Hydrosol or Colloidal Osmium** is readily prepared by reducing potassium osmate, K₂OsO₄, with hydrazine hydrate in the presence of some protective colloid such as gum acacia ² or lysalbate (or protalbate) of sodium.³ The reduction may be effected with acrolein ⁴ if desired.

Colloidal osmium may also be obtained by reduction of colloidal osmium dioxide. The last named is prepared (see p. 220) by reduction with hydrazine hydrate of potassium osmate solution suspended in lanolin, which serves as protective colloid. The product is dissolved in petroleum, precipitated with alcohol and reduced in a current of hydrogen at 50° to 60° C. A solution containing 21 per cent. of osmium has been obtained in this manner.⁵

Colloidal osmium readily undergoes oxidation; it catalytically assists the oxidation of unsaturated compounds by gaseous hydrogen. In this respect it is stated to be even more effective than the finely divided metal,⁶ but less active than either platinum or iridium. Carbon monoxide combines with oxygen, yielding the dioxide, when shaken at ordinary temperatures with the hydrosol of osmium.⁷

**Catalytic Activity of Finely Divided Osmium.**—In the finely divided condition metallic osmium possesses marked catalytic activity.⁸ At 40° to 50° C. it causes hydrogen and oxygen to unite with explosive violence.⁹ It has proved to be a very effective catalyst in the preparation of ammonia by synthesis from its elements under a pressure of 185 atmospheres and at a temperature of 880° to 1000° C.¹⁰ Osmium obtained by ignition of ammonium chlorosmate in hydrogen, when mixed with certain unsaturated organic substances such as cyclohexene, either alone or diluted with acetone, and exposed to an atmosphere of oxygen, catalytically assists their oxidation. This property is not shared under these conditions by the other platinum metals, although tellurium exhibits a certain degree of activity.¹¹

**Atomic Weight.**—*Approximate Atomic Weight.*—Several considerations lead us to the conclusion that the atomic weight of osmium is of the order of 191. The chief reasons may be summarised as follows:

1. Analyses of and vapour density measurements with osmium tetroxide and osmium octafluoride indicate that the osmium in the molecules of these two compounds has a weight of approximately 190.

3. Paal and Amberger, Ber., 1907, 40, 1392, 2201.
6. Willstatter and Sonnenfeld, Ber., 1914, 47, 2801.
11. Willstätter and Sonnenfeld, Ber., 1913, 46, 2952.
This sets a superior limit to the atomic weight of osmium, which might, however, be a submultiple of this value.

(2) The specific heat of osmium is 0.0811. Assuming, therefore, a mean atomic heat of 6.4, the atomic weight of the metal, according to Dulong and Petit's Law, is approximately 200.

(3) Osmium bears a close resemblance to ruthenium in many of its chemical properties; in fact, in certain respects, such as the formation of tetroxides, these two elements are absolutely unique amongst the metals of the platinum group.

Furthermore, a distinct gradation in properties can be traced as we pass from osmium, through iridium to platinum.

There seems little reason to question, therefore, the propriety of placing osmium as the first member of the third series of triads in Group VIII. This postulates an atomic weight intermediate between 184 (at. wt. of tungsten) and 198.1 (at. wt. of iridium), but nearer to the latter value, inasmuch as an intermediate element between tungsten and osmium is missing from Group VII.

(4) Alkali hexachlorosmates are isomorphous with the corresponding derivatives of palladium, iridium, and platinum, and may therefore be assumed, by application of the Law of Mitscherlich, to have the general formula $M_2\text{OsCl}_6$.

Again, potassium osmocyanide is isomorphous with potassium ferrocyanide and potassium ruthenocyanide, and may therefore be judged to have the formula $K_4\text{Os}(CN)_6 \cdot 3\text{H}_2\text{O}$.

Analyses of these compounds indicate that the atomic weight of osmium is 190.9.

**Exact Atomic Weight.**—The early determinations, by Berzelius\(^1\) and Frémy\(^2\), gave very high values for the atomic weight of osmium. Berzelius analysed potassium chlorosmate by reducing the heated salt in a stream of hydrogen, and separating and weighing the osmium and potassium chloride in the residue, his result being as follows\(^3\):

\[
2\text{KCl} : \text{Os} : 100.00 : 183.42 \text{ whence } \text{Os} = 198.9
\]

Frémy's value was $\text{Os} = 199.7$, derived from the analysis of osmium tetroxide.

That these values are much higher than the correct one was foretold by Mendéléeff, and confirmed by Seubert in 1888. The latter chemist showed the substantial accuracy of his results in a second series of experiments, published in 1891.\(^4\)

Seubert analysed two salts, namely, ammonium and potassium chlorosmate. The former was heated in a stream of hydrogen, the residual osmium weighed, the volatile chlorides collected, and the chlorine contained therein determined as silver chloride.

\[
\begin{align*}
6 \text{expts. } (\text{NH}_4)_2\text{OsCl}_6 & : \text{Os} : 100.000 : 43.459 \text{ whence } \text{Os} = 191.25 \\
4 \text{expts. } 6\text{AgCl} & : (\text{NH}_4)_2\text{OsCl}_6 : : 100.000 : 51.283 \text{ whence } \text{Os} = 192.23
\end{align*}
\]

The latter was first analysed by reduction in a stream of hydrogen, the hydrogen chloride produced being determined by conversion into

\(^3\) The antecedent data employed in the calculations in this section are as follow: $O = 16.000$, $N = 14.008$, $H = 1.00782$, $Cl = 35.457$, $Ag = 107.880$, $K = 39.100$.
\(^4\) Seubert, *Ber.*, 1888, 21, 1839; *Annalen*, 1891, 261, 257.
silver chloride; the residual osmium plus potassium chloride was weighed, the potassium chloride dissolved out, recovered by evaporation, and weighed separately.

2 expts.  \( K_2\text{OsCl}_3 : 2\text{KCl} : 100-000 : 30-987 \), whence \( Os = 190.27 \)
2 expts.  \( 4\text{AgCl} : K_2\text{OsCl}_3 : 100-000 : 84-097 \), \( Os = 191.23 \)

In a second method of analysis employed with this salt the weighed mixture of osmium and potassium chloride, obtained as before, was ignited in a boat in a platinum tube until the potassium chloride had volatilised, a current of hydrogen passing through the tube during the experiment. The residual osmium was then weighed:

9 expts.  \( K_2\text{OsCl}_3 : \text{Os} : 100-000 : 39.353 \), whence \( Os = 190.38 \)
7 expts.  \( K_2\text{OsCl}_3 : 2\text{KCl} : 100-000 : 30.981 \), \( Os = 191.14 \)

In 1912 Seybold\(^1\) published two series of analyses of ammonium chlorosmate, the osmium being determined:

(i) 5 expts.  \( (\text{NH}_4)_2\text{OsCl}_4 : \text{Os} : 100-000 : 43.212 \), whence \( Os = 189.4 \)
(ii) 3 expts.  \( (\text{NH}_4)_2\text{OsCl}_4 : \text{Os} : 100-000 : 43.437 \), \( Os = 191.1 \)

Seybold considers that the second series of analyses is vitiated owing to absorption of oxygen by the osmium.

The Table given by the International Committee for 1918 gives

\( Os = 190.9 \).

It will be clear that neither Seubert's nor Seybold's results are of the high standard reached in many modern atomic weight researches. Further determinations of this atomic weight are urgently needed, the value in current use being stated more precisely than is justified by the evidence at present available.

**Uses.**—Osmium has been used in the manufacture of filaments for certain electric lamps on account of its high infusibility, for, next to tungsten, it is the most refractory of metals.

Otherwise the metal is of but little commercial importance. Certain of its compounds, notably osmic acid, are used in microscopv.

**Alloys.**—The most important alloy of osmium is osmiridium or iridosmine, which occurs in nature in platinum ores, as has already been mentioned.\(^2\) Two varieties are known, namely, nevyanskite, containing over 40 per cent. of iridium, and siserskite, containing 80 per cent. or less of that metal.\(^3\) Osmiridium is exceptionally resistant to acid attack, and is non-magnetic. It is used in tipping gold pen nibs. No definite compound of osmium and iridium is known, however. In fact osmium does not appear to form compounds with any metals. It dissolves in zinc,\(^4\) and undoubtedly forms an amalgam with mercury, since the last named, in contact with osmium tetroxide, wets glass, containing vessels becoming rapidly silvered.\(^5, 6\) With iron an alloy is formed capable of taking a temper.\(^7\) Osmium, when finely divided,

---

2. See p. 208, where analyses of the alloy from various sources are given.
alloys with gold, but the product is attacked by aqua regia. Alloys with copper have been prepared.

OSMIUM AND FLUORINE

Until 1913, no definite fluoride of osmium had been isolated, although it was known that, upon warming osmium in fluorine, combination takes place. Furthermore, on heating osmic acid with an alcoholic solution of hydrogen fluoride, a dark powder has been obtained, which appears to be an oxyfluoride.

In 1913, however, Ruff and Tschirch published an account of their very interesting researches into the nature of the products formed when osmium is heated in fluorine. They showed that three fluorides are capable of existence, namely, the tetra-, hexa-, and octa-fluoride respectively. The last named is interesting as definitely establishing the octavalent nature of osmium.

The osmium was obtained by reduction of the dioxide in a mixture of hydrogen and carbon dioxide, the most reactive metal being obtained at lower reduction temperatures, namely, about 250°C. Upon passing fluorine over, a mixture of the fluorides was obtained, the relative proportions varying according to the temperature, the rate of flow of the fluorine current, and the particular physical condition of the osmium.

For example, by employing a temperature of 250°C and a rapid stream of fluorine, a very reactive osmium preparation was found to yield a high percentage of Osmium Octafluoride, OsF₈. This, being the most volatile of the products, is collected in a vessel cooled in a mixture of solid carbon dioxide and alcohol, under which conditions it yields a yellow, solid sublimate. It melts at 34-5°C to a yellowish red liquid. Its vapour is colourless, has a characteristic odour and metallic taste: it attacks the mucous membranes of the nose and eyes. In moist air the vapour yields a white cloud.

The vapour pressures for different temperatures are as follow:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Pressure mm.</th>
<th>Temperature °C</th>
<th>Pressure mm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>38-0</td>
<td>552-5</td>
<td>48-5</td>
<td>655-6</td>
</tr>
<tr>
<td>40-8</td>
<td>594-5</td>
<td>47-8</td>
<td>757-5</td>
</tr>
<tr>
<td>42-0</td>
<td>634-2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mean vapour density is 177-5 (H = 1), that calculated for the formula OsF₈ being 172.

When heated in a platinum tube, osmium octafluoride begins to decompose at 225°C, but the extent of decomposition only becomes appreciable at about 400°C.

Organic substances are violently attacked by osmium octafluoride, and the skin burnt. In aqueous solution the salt is colourless and

1 Tennant, *Phil. Trans.*, 1804, 94, 411.
3 Ruff and Tschirch, *Ber.*, 1913, 46, 929.
partially hydrolysed, the solution having the odour of the tetroxide. In sodium hydroxide solution a yellowish red colour is obtained, characteristic of perosmates.

With alkali fluorides double salts are produced, the compositions of which are as yet unknown. They are less easily reduced, however, than the free octafluoride. Sodium hydroxide decomposes them with evolution of ozone.

**Osmium Hexafluoride**, OsF₆—The proportion of this fluoride in the mixture obtained by passage of fluorine over reduced osmium at 25° C. is increased by reducing the rate of passage of the fluorine. The octafluoride, being most volatile, passes farther along from the furnace, being collected in a cooled receiver. The hexafluoride condenses in the tube close by where it leaves the furnace. In order to completely free it from octafluoride it is gently warmed to 50° C. under a pressure of 20 mm., when it sublimes and condenses on a cool part of the tube as a light green crystalline deposit. It has not been obtained in a perfectly pure condition as it proved to be extremely difficult to obtain entirely free from oxide. Its boiling-point is approximately 202° to 205° C., whilst its melting-point lies between 50° and 120° C.

The latter constant could not be obtained accurately as the fluoride becomes black upon heating in contact with glass. Osmium hexafluoride is decomposed by water, yielding hydrofluoric acid and oxides of osmium. In caustic soda it gives a reddish yellow colour similar to that of the hexachlorosmates.

**Osmium Tetrafluoride**, OsF₄, is obtained by passing fluorine over osmium at 280° C., the osmium having been reduced from the dioxide at red heat and rendered thereby less reactive. The small quantities of the higher fluorides simultaneously formed are removed by heating the tube, in which fluorination has been effected, to 100° C. in an atmosphere of nitrogen under low pressure.

The tetrafluoride has not been isolated in the pure state. It dissolves in water, and by adding hydrogen fluoride and neutralising with potassium hydroxide, crystals are obtained upon concentration, consisting probably of *Potassium Fluorosmate*, K₂OsF₆.

**OSMIUM AND CHLORINE**

**Osmium Dichloride**, OsCl₂, was stated to result when osmium is heated in chlorine, but it is very doubtful if it has ever been successfully obtained in this way.

In 1910, Ruff and Bornemann definitely proved that osmium dichloride is capable of existence, for they prepared it by heating the trichloride to 500° C. under reduced pressure.

Obtained in this manner, osmium dichloride is a dark brown powder, practically insoluble in water, but attacked by prolonged boiling with water, yielding a pale yellow solution. Concentrated nitric acid and aqua regia slowly attack it, giving osmium tetroxide; whilst concentrated alkali solutions slowly attack it in the cold, yielding clear but deep brown solutions.

Unlike platinum dichloride, osmium dichloride does not yield chlor-

---

OSMIUM AND ITS COMPOUNDS

osmous acid, $H_2OsCl_4$, analogous to chlor-platinoïd acid, $H_2PtCl_4$, with concentrated hydrochloric acid.

**Osmium Trichloride**, $OsCl_3$, is obtained by heating osmium, obtained by reduction of the dioxide in hydrogen, in chlorine at about 1050° C., and cooling the vapour rapidly. It then contains some admixed osmium tetrachloride.

A purer product is prepared by igniting ammonium chlorosmate, $(NH_4)_2OsCl_6$, in chlorine at 350° C. Osmium trichloride, obtained by the foregoing method, is a brownish black, crystalline powder, which is hygroscopic and readily soluble in water, yielding a dark brown solution. This solution is stable even when boiled, although it possesses a slightly acid reaction.

The *trihydrate*, $OsCl_3\cdot3H_2O$, is obtained as follows: osmic acid on prolonged boiling with hydrochloric acid and a little alcohol yields, on evaporation, red crystals of composition $OsCl_3\cdot7H_2O$, which are attacked by moist air yielding an olivc-green mass. On solution in alcohol, and addition of potassium chloride, crystals of potassium chlorosmate, $K_2OsCl_6$, are obtained, the filtrate yielding, on evaporation, dark green crystals of the hydrated trichloride, $OsCl_3\cdot3H_2O$. These, on heating in a current of hydrogen, are reduced to osmium, hydrogen chloride and water vapour being evolved. At the same time a minute trace of yellow sublimate is obtained, which Morahé and Wischin suggest may be a higher chloride, possibly the *octachloride*, $OsCl_6$.

*Hexachlorosmites*, $M_3OsCl_6$ or $M_2OsCl_5\cdotMCl$

Osmium trichloride yields a series of double salts known as *osmochlorides* or *chlorosmites*, $M_3OsCl_6$. Of these the most important are the potassium and ammonium salts.

**Potassium Chlorosmite**, $K_3OsCl_6\cdot3H_2O$, is obtained as dark red crystals, along with the colourless crystals of potassium and ammonium chloride by addition of ammonia to a solution of osmium tetroxide in aqueous potassium hydroxide, and subsequent saturation with hydrogen chloride.

The crystals effloresce in air. They dissolve in water to a red solution which possesses an astringent taste, but which becomes sweet and unpleasant upon standing.

The crystals dissolve in alcohol, but not in ether. Alkalies and alkali peroxides precipitate the hydrated sesquioxide from the aqueous solution.

**Ammonium Chlorosmite**, $(NH_4)_2OsCl_6\cdot3H_2O$, results when hydrogen chloride is passed into a solution of osmium tetroxide in hydrochloric acid. The red liquid is evaporated with ammonium chloride, when crystals of the same colour are obtained.

**Osmium Tetrachloride**, $OsCl_4$, is obtained as a reddish brown sublimate when metallic osmium is heated in chlorine (Berzelius) between 650° and 700° C.¹

When resublimed in chlorine it condenses into a black mass of the same composition. On volatilisation it yields a yellow vapour. It is neither hygroscopic nor soluble in the usual solvents, save the powerful

oxidising acids. Water has no action upon it unless the two are left in contact for a prolonged period, when hydrolysis gradually sets in, hydrochloric acid and osmium dioxide resulting.

*Hexachlorosmates, M₂OsCl₆*

Osmium tetrachloride yields a series of double salts known as *osmichlorides* or *chlorosmates, M₂OsCl₆*. Of these the potassium, sodium, and ammonium salts are best known.

**Potassium Chlorosmate, K₂OsCl₆**, is obtained by prolonged boiling of osmic acid with hydrochloric acid, and subsequent evaporation of the solution with potassium chloride. Dark brown crystals of the chlorosmate separate out, leaving osmium trichloride in solution.

Potassium chlorosmate may also be obtained by heating the finely divided metal with potassium chloride in chlorine,¹ by double decomposition of the sodium salt with potassium chloride,² or by the action of hydrochloric acid on potassium osmyl oxynitrite.³ It is soluble in water, yielding a yellow solution from which alcohol precipitates it as a red crystalline powder. The crystals are deep red octahedra, isomorphous with the corresponding palladium, iridium, and platinum analogues.

When ignited, the dry salt yields a residue of metallic osmium and potassium chloride.

The solution decomposes on warming, the tetroxide being produced and a black powder deposited.

From the solution alkalies and ammonia precipitate the hydrated dioxide, whilst excess of ammonia yields osmium diammine hydroxide. Ferrous sulphate and alkali formates reduce the salt, liberating metallic osmium.

**Sodium Chlorosmate, Na₂OsCl₆·2H₂O**, may be obtained in a similar manner to the potassium salt. Rosenheim and Sasserath ² described a new method, according to which sodium osmisulphite is gradually heated up in a current of dry hydrogen chloride. The mass becomes black at first, then froths up in consequence of the escape of sulphur dioxide; finally a reddish brown product remains behind, which in air immediately becomes brick-red. It dissolves in a small quantity of water to a green solution ⁴ which on concentration over sulphuric acid yields long orange-coloured prisms. When boiled with a concentrated solution of sodium hydrogen sulphite, sodium chlorosmate yields the osmisulphite,⁵ Na₂Os(SO₃)₂·8H₂O.

**Ammonium Chlorosmate, (NH₄)₂OsCl₆**, is prepared by double decomposition of the sodium salt with ammonium chloride.¹ Upon recrystallisation, brown octahedra are obtained.

Methyl and ethyl ammonium chlorosmates have been prepared.³

**Silver Chlorosmate, Ag₂OsCl₆**, results as a green precipitate on adding silver nitrate solution to one of sodium or potassium chlorosmate.²

The chlorosmates of *Rubidium and Caesium* have also been prepared.⁶ They are soluble in cold water, but the solutions decompose upon

⁴ The green colour is probably due to traces of osmium trichloride.
exposure to air, depositing a black powder. The salts readily dissolve in hydrochloric acid.

**Organic Chlorosmates** are described by Gutbier and his co-workers.1

**Sodium Osmium Hexachloride,** \( \text{Na}_8 \text{OsCl}_{12} \) or \( \text{OsCl}_4 \cdot 6\text{NaCl} \), has been prepared by Rosenheim and Sasserath2 by passing dry hydrogen chloride over sodium osmisulphite, gently warming the while. A black reaction product is obtained, which is dissolved in a small quantity of water and recrystallised over sulphuric acid. Bright, coppery leaflets are obtained consisting of sodium osmium hexachloride, contaminated with a small quantity of sulphite. Addition of potassium chloride to the solution of the salt does not yield the corresponding potassium salt, but potassium chlorosmate; neither could the potassium or ammonium salt be obtained by the direct method.

**Osmium Octachloride,** \( \text{OsCl}_8 \), appears to be formed in small quantity when chlorine is allowed to act upon heated osmium 3; as also when hydrated osmium trichloride, \( \text{OsCl}_3 \cdot 3\text{H}_2\text{O} \), is heated in a current of hydrogen. In this latter case, what is believed to be the octachloride is formed in minute quantities as a yellow sublimate.4

**OSMIUM AND BROMINE**

**Bromides of Osmium.**—Osmium is not affected by exposure to bromine vapour even under the influence of heat. By warming osmic acid, \( \text{H}_2\text{OsO}_4 \), with hydrobromic acid in the presence of alcohol (to prevent oxidation to the volatile tetroxide), a brown solution was obtained by Morah and Wischin.4 This was concentrated *in vacuo* over sulphuric acid and potassium hydroxide, the latter to absorb the hydrobromic acid, and upon recrystallisation dark reddish brown hygroscopic needles were obtained. These were readily soluble in water and alcohol, from which they could be recrystallised unchanged in the cold. The results of analysis agreed well with the formula \( \text{Os}_2\text{Br}_9 \cdot 6\text{H}_2\text{O} \), indicating, probably, a mixture of the tri- or tetra-bromide with some higher bromide. Concentration of the solution on the water-bath results in the formation of an *oxybromide* of unknown constitution.

**Potassium Bromosmate,** \( \text{K}_2\text{OsBr}_8 \), is obtained by double decomposition of the sodium salt with potassium bromide,2 as a brownish black crystalline powder of coppery hue. From dilute solution octahedral crystals are obtainable. They are brownish black in colour, opaque, and metallic in appearance.5 The salt is difficultly soluble in water.2

**Sodium Bromosmate,** \( \text{Na}_2\text{OsBr}_4 \cdot 4\text{H}_2\text{O} \), may be prepared by the action of dry hydrogen bromide on sodium osmisulphite, \( 3\text{Na}_2\text{O} \cdot \text{OsO}_2 \cdot 4\text{SO}_2 \cdot 5\text{H}_2\text{O} \) (see p. 280), or better by decomposition of the same with aqueous hydrogen bromide, of density 1-45.2 A deep purple-red solution is obtained from which long, dark brown prisms crystallise out, possessed of a metallic appearance.

3 Claus, *Bull. Acad. Soc. PÉtrograd*, 1863, 6, 150.
5 Rosenheim, *ibid.*, 1900, 24, 420. Crystallographic data are given. See also Sachs, *Zeitsch. Kryst.*, 1901, 34, 162.
Ammonium Bromosmate, \((\text{NH}_4)_2\text{OsBr}_6\), is prepared in the same manner as the potassium salt. On crystallisation from dilute solution octahedral and tetrahedral forms are obtained.\(^1\) Methyl and ethyl ammonium bromosmates have been prepared.\(^2\)

**Silver Bromosmate**, \(\text{Ag}_2\text{OsBr}_6\), results as a flocculent, indigo precipitate by addition of silver nitrate solution to one of the sodium salt.\(^1\)

**Organic Bromosmates** have been prepared.\(^3\)

**OSMIUM AND IODINE**

**Osium Hydriodide**, \(\text{OsI}_3.2\text{HI}\), is stated by Alvarez\(^4\) to result as an emerald-green substance by the interaction of hydrochloric acid, potassium iodide, and osmium tetroxide:

\[
\text{OsO}_4 + 10\text{HCl} + 10\text{KI} = \text{OsI}_3.2\text{HI} + 4\text{H}_2\text{O} + 10\text{KCl} + 3\text{I}_2.
\]

It is soluble in water, readily reducing acidulated permanganate and chromate solutions. It is bleached in contact with oxidising acids, but is very stable in concentrated solutions of salts, with which it forms iodosmites. The green colour of the iodide is of such intensity that its formation serves as a delicate colorimetric test for the presence of osmium. The test is carried out as follows:

The solution supposedly containing osmium tetroxide is treated with a saturated solution of calcium chloride, a little potassium iodide and phosphoric acid, and the colour noted.

**Osium Tetra-iodide**, \(\text{OsI}_4\), was obtained by Moraht and Wischin\(^5\) by heating on the water-bath osmic acid, \(\text{H}_2\text{OsO}_4\), and a concentrated aqueous solution of hydrogen iodide. The osmic acid slowly dissolves, yielding a deep brown solution, which is stable in the cold. Concentration in vacuo over sulphuric acid and caustic potash (to absorb the hydrogen iodide), and subsequent recrystallisation, yields rhombohedral crystals violet-black in colour, and of metallic appearance. They are hygroscopic, readily soluble in alcohol and water, yielding a reddish brown solution stable in the cold, but one that readily decomposes on warming with precipitation of a dark oxy-iodide.

**Potassium Iodosmate**, \(\text{K}_2\text{OsI}_5\), is readily prepared\(^2\) by treating potassium osmyl oxynitrite with a fairly concentrated solution of hydriodic acid:

\[
\text{K}_2(\text{OsO}_3)(\text{NO}_2)_2 + 8\text{HI} = \text{K}_2\text{OsI}_5 + \text{I}_2 + 2\text{HNO}_2 + 3\text{H}_2\text{O}.
\]

The reaction is vigorous, nitrous fumes being disengaged, as also iodine vapour. On filtering the brownish violet solution and allowing to stand, crystals of potassium iodosmate separate out as dark violet octahedra. The salt is not very soluble in water, but more so than the brom- and chlor- osmates, and the solution rapidly decomposes, although the presence of a little free hydriodic acid renders it stable. It may be heated to 200° C. in hydrogen without loss in weight, but in the neighbourhood of 300° C. hydrogen iodide is evolved.

---

Ammonium Iodosmate, \((\text{NH}_4)_2\text{OsI}_6\), prepared in a similar manner to the potassium salt crystallises in bluish black octahedra.

OSMIUM AND OXYGEN

**Osmium Monoxide**, \(\text{OsO}_2\), results as a greyish black powder when a mixture of the sulphite, \(\text{OsSO}_3\), and sodium carbonate is heated in a current of carbon dioxide.\(^2\) It is insoluble in acids.

**Osmium Dihydroxide, Hydrated Osmium Monoxide**, \(\text{Os(OH)}_2\), is prepared as an unstable, bluish black precipitate on warming osmium sulphite with a concentrated solution of potassium hydroxide.\(^2\)

**Osmium Sesquioxide**, \(\text{Os}_2\text{O}_3\), is obtained by heating salts of trivalent osmium with sodium carbonate in a current of carbon dioxide. It also results when an excess of osmium tetroxide is reduced by heating with finely divided osmium.\(^3\)

The sesquioxide is a dark powder, insoluble in acids. It is obtained in the hydrated condition, \(\text{Os}_2\text{O}_3\cdot2\text{H}_2\text{O}\), as a reddish brown precipitate on adding an alkali to an aqueous solution of an osmochloride.\(^2\)

**Osmium Dioxide**, \(\text{OsO}_4\), results when salts of tetravalent osmium are heated with sodium carbonate in a current of carbon dioxide, and by heating finely divided osmium in the vapour of osmium tetroxide.\(^4\)

Osmium dioxide may also be obtained in the anhydrous condition by ignition of potassium osmiamate, \(\text{OsNO}_3\text{K}\), in vacuo at 350° C.,\(^5\) or by heating the hydrate, \(\text{OsO}_2\cdot2\text{H}_2\text{O}\), to a little below 200° C. in an inert gas such as nitrogen or carbon dioxide. Obtained in this manner its density\(^4\) is 7.71. Further heating to 400° C. changes the colour progressively from bluish black, the colour of the dihydrate, to brown, and slightly increases the density. At about 460° C. the dioxide begins to decompose into osmium and its tetroxide according to the equation:

\[
2\text{OsO}_2 = \text{Os} + \text{OsO}_4,
\]

but by heating the dioxide in the vapour of tetroxide this decomposition is retarded until a temperature of about 650° C. is arrived at. The dioxide then has a density of 7.91, and consists of copper-coloured crystals of octahedral and hexahedral forms.\(^4\) They are insoluble in acids, but are readily reduced by hydrogen.

**Pyrophoric Osmium Dioxide**.—The oxide prepared by reduction of alkali osmates with alcohol or by hydrolysis of ammonium chlorosmate is not pure, but contains small quantities of organic substances or alkalies. When dry it is liable to ignite upon exposure to air, and even to detonate if warmed \(^4\) to 300° C. directly it meets the air.

**Hydrated Osmium Dioxide** exists in two stages of hydration. The dihydrate, \(\text{OsO}_2\cdot2\text{H}_2\text{O}\), is obtained by the reduction of alkali osmates with alcohol:

\[
\text{K}_2\text{OsO}_4 + 2\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH} = \text{OsO}_2\cdot2\text{H}_2\text{O} + 2\text{KOH} + \text{CH}_3\cdot\text{CHO}.
\]

It also results upon hydrolysing an alkali chlorosmate, thus:

\[
\text{K}_2\text{OsCl}_6 + 4\text{H}_2\text{O} = \text{OsO}_2\cdot2\text{H}_2\text{O} + 2\text{KCl} + 4\text{HCl}.
\]

\(^1\) Wintrebert, loc. cit.
\(^3\) Deville and Debray, *Compt. rend.*, 1876, 82, 1077.
\(^4\) Ruff and Rathshurg, *Ber.*, 1917, 50, 484.
The oxide is thrown out in colloidal form, but addition of electrolytes to its neutral solution effects its precipitation. The method may be varied by heating potassium chlorosmate with pure sodium hydroxide in solution in the absence of air, on the water-bath.

When dried over sulphuric acid it has the composition $\text{OsO}_2\cdot2\text{H}_2\text{O}$. It gradually oxidises in air, yielding the tetroxide. When heated to 120° C. in an inert gas it loses a molecule of water, being converted into the monohydrate, $\text{OsO}_2\cdot\text{H}_2\text{O}$.

**Colloidal Osmium Dioxide.**—It has already been mentioned that osmium dioxide, obtained either by reduction of an alkali osmate with alcohol or by hydrolysis of an alkali chlorosmate, is precipitated in the colloidal form.

A more permanent colloidal solution is obtained in the presence of a protective colloid. It may be prepared, for example,\(^1\) by impregnation of lanolin with a solution of potassium osmate, and subsequent reduction with hydrazine hydrate. The lanolin serves as the protective colloid. The product is dissolved in light petroleum and may be precipitated by addition of alcohol. By heating the precipitate to 50° C. in hydrogen, reduction to colloidal metallic osmium takes place.

**Osmic Acid, $\text{H}_2\text{OsO}_4$,** does not appear to have been prepared. The black compound obtained by acting upon potassium osmate with dilute nitric acid was believed by Morath and Wischin\(^2\) to be correctly represented by the formula $\text{H}_2\text{O}\cdot\text{OsO}_3$ or $\text{H}_2\text{OsO}_4$, but this has not been confirmed by the more recent researches of Ruff and Bornemann,\(^3\) who regard the product as the hydrated dioxide. Further research is necessary to elucidate this point.

**Potassium Osmate, $\text{K}_2\text{OsO}_4\cdot2\text{H}_2\text{O}$,** results when a solution of the tetroxide in aqueous potassium hydroxide is reduced with alcohol.\(^4\) The solution acquires a red colour from which the salt separates. On slow recrystallisation, garnet-red to black octahedra\(^5\) are obtained, permanent in dry air, but decomposing in moist air as also in solution, yielding the tetroxide and lower oxides.

Potassium osmate may be obtained in a pure state by fusing osmium with potassium nitrate and hydroxide, dissolving the melt in water, and precipitating with alcohol. The potassium osmate thus obtained has a greyish violet colour, and is not quite pure. It is therefore heated to 120° C. with a mixture of sulphuric acid and chromium trioxide, whereby osmium tetroxide is produced. This volatilises and is collected in 10 per cent. potash solution, from which it is obtained in a pure, crystalline form on addition of alcohol.\(^6\)

The solution of the pure salt is not as unstable as was originally believed by earlier investigators,\(^6\) since it may be kept in the cold exposed to sunlight for many days without serious decomposition.\(^6\) On warming, decomposition is accelerated, and the odour of osmium tetroxide becomes pronounced.\(^4\)

At 200° C. the crystals become anhydrous in an inert atmosphere.

Osmates of Sodium and Barium have also been prepared.

---

Osmium Tetroxide, $\text{OsO}_4$, frequently but incorrectly known as osmic acid, is the highest oxide of osmium known, and is formed in a variety of ways. Finely divided metallic osmium slowly oxidises in air to the tetroxide, and more rapidly on heating in air or, better, in oxygen.\(^1\) At high temperatures the compact metal yields vapours of the volatile tetroxide, and this affords a useful means of quantitatively separating osmium from its iridium alloy (p. 338).

The tetroxide is also formed by oxidation of the lower oxides with nitric acid. The metal itself, if it has not been previously ignited, may also be oxidised with nitric acid to the tetroxide. When purified by sublimation, osmium tetroxide is obtained as transparent needles,\(^2\) which soften at the temperature of the hand and melt at 45° C.\(^3\) They slowly dissolve in water to a colourless solution, which is used in microscopic work for staining purposes, the oxide being reduced to the metal. The solution possesses a burning taste, but does not redden litmus. It is, however, coloured yellow, brown, green, and, finally, indigo blue by sulphur dioxide. The crystals also dissolve in alcohol and in ether.

The tetroxide readily sublimes on heating. When fused it boils at 100° C., yielding a vapour of density 8.89 (air = 1)\(^4\) or 128 (H = 1), the theoretical requirement for the formula $\text{OsO}_4$ being 127.5 (H = 1). The vapour is very penetrating and exceedingly poisonous, producing temporary blindness and other alarming symptoms. If inhaled, the best antidote appears to be hydrogen sulphide, which neutralises the action of the tetroxide on the respiratory organs.\(^5\)

The vapour pressures of osmium tetroxide at various temperatures are as follow\(^6\):

<table>
<thead>
<tr>
<th>Temperature °C.</th>
<th>95</th>
<th>115</th>
<th>125</th>
<th>135</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, mm.</td>
<td>275</td>
<td>182</td>
<td>640.4</td>
<td>779</td>
</tr>
</tbody>
</table>

Mild reducing agents such as alcohol convert the tetroxide into lower oxides of osmium. When thrown on to red-hot charcoal it deflagrates. Its vapour, when passed over glowing copper turnings, is reduced, metallic osmium being deposited on the copper. If a current of hydrogen gas is simultaneously passed through, the copper oxide is reduced as rapidly as formed, and the alteration in weight of the copper is due entirely to the deposit of metallic osmium. This affords a convenient method of quantitatively estimating osmium with very considerable accuracy.\(^7\)

Osmium tetroxide catalytically assists the oxidation of certain oxidisable substances. For example,\(^8\) a mixture of 15 grams of arsenic with 10 grams of potassium chlorate in 50 c.c. of water remains unaltered even after addition of a few drops of dilute sulphuric acid. Upon introducing a trace of osmium tetroxide (c. 0.015 gram) in solution, the temperature immediately rises, the arsenic being rapidly oxidised to...

---


\(^{3}\) Ruff and Tschirch, *Ber.*, 1913, 46, 929; Svanberg (*Jahresber.*, 1847, 26, 181) gave 40° C.


\(^{6}\) Ruff and Tschirch, *Ber.*, 1913, 46, 929.


\(^{8}\) K. A. Hofmann, *Ber.*, 1912, 45, 3329.
arsenic acid. Hydrazine sulphate may be oxidised in a similar manner, the reaction proceeding quantitatively and admitting of exact measure-
ment by collection of the liberated nitrogen.\textsuperscript{1} This activity is attributed to the formation of an additive compound between osmium tetroxide and the chlorate, the complex thus formed acting as the oxidiser. That it is caused by the formation of a higher oxide of osmium seems unlikely, since osmium tetroxide does not take up oxygen from solutions of chlorates. Furthermore, a purely catalytic decomposition of the chlorate seems improbable, since osmium tetroxide does not appreciably influence the rate of decomposition of either the solid chlorate or its solutions.

On the other hand, osmium tetroxide may be used to catalytically assist the reduction or hydrogenation of unsaturated oils like linseed or cotton-seed oils.\textsuperscript{2} The oil is mixed with a small quantity of the tetroxide, hydrogen passed through, and the whole warmed, just as when nickel or its oxides is used as catalyst (see p. 95). The osmium can be recovered, by treatment with charcoal, in the form of its dioxide, a colloidal solution of which is frequently formed in the oil by the reduction of the tetroxide during the process.

Aqueous solutions of osmium tetroxide are readily reduced by the introduction of practically any metal except those known as the precious metals.\textsuperscript{3} Thus zinc, silver, mercury, etc., effect the precipitation of metallic osmium from acidulated solutions in a very pure form. In the last-named case an amalgam is produced from which the osmium is obtained by distilling off the mercury. Ferrous sulphate and stannous chloride\textsuperscript{4} also reduce the tetroxide solutions, but hydrogen,\textsuperscript{5} sulphur and selenium\textsuperscript{6} appear to have no action under ordinary conditions. Sulphur dioxide reduces the solution to osmium sulphite, whilst potassium iodide reduces it to dioxide with liberation of iodine—a reaction that may be utilised in the volumetric determination of osmium.\textsuperscript{7}

The acidic properties of osmium tetroxide are illustrated by the formation of definite compounds with the alkali hydroxides. These are crystalline, orange or brown in colour, and readily soluble in water, yielding strongly hydrolysed solutions. Of these the following derivatives have been obtained\textsuperscript{8}: OsO\textsubscript{4}.2KOH, OsO\textsubscript{4}.RbOH, OsO\textsubscript{4}.CsOH, and 20\textsubscript{5}O\textsubscript{4}.CsOH.

Osmium tetroxide does not liberate iodine from neutral solutions of potassium iodide.\textsuperscript{9}

**OSMYL DERIVATIVES**

Salts containing the group OsO\textsubscript{2} in the acid radicle are known as osmyl derivatives, and have the general formula:

$$M_2(OsO_2)X_4.$$  

\textsuperscript{1} Further examples are discussed by K. A. Hofmann, Erhart, and Schneider, Ber., 1913, 46, 1657.

\textsuperscript{2} F. Lehmann, Arch. Pharm., 1913, 251, 152; Norman and Schick, ibid., 1914, 252, 208.

\textsuperscript{3} Tennant, Phil. Trans., 1804, 94, 411; Fischer, Pogg. Annalen, 1828, 12, 499; Berzelius, Ann. Chem. Phys., 1829, 40, 261.

\textsuperscript{4} Rose, Traité de chimie analytique, 1859, 1, 220.

\textsuperscript{5} Phillips, Zeitsch. anorg. Chem., 1894, 6, 231.

\textsuperscript{6} Fischer, loc. cit.

\textsuperscript{7} See p. 338.

\textsuperscript{8} Tschugaev, Compt. rend., 1918, 167, 162.

\textsuperscript{9} Orloff, Chem. Zeit., 1907, 31, 1063.
where M stands for a monovalent metal and X for a monovalent acid radical. These substances have been carefully studied by Wintrebert.\(^1\)

Of the various osmyl derivatives the potassium salts may be regarded as the most important, since from them it is easy to prepare the corresponding salts of silver, barium, etc., by simple double decomposition.

The potassium salts may be obtained by the action of a suitable reducing agent upon osmium tetroxide in the presence of a simple potassium salt or its hydroxide. Thus, for example, potassium osmyl nitrite results when the tetroxide is reduced by nitric oxide in the presence of potassium nitrite solution:

\[
\text{OsO}_4 + 2\text{NO} + 2\text{KNO}_2 = \text{K}_2(\text{OsO}_2)(\text{NO}_2)_4.
\]

On the other hand, the corresponding oxalate may be produced by treating a solution of the tetroxide in potassium hydroxide with excess of oxalic acid. Thus:

\[
\text{OsO}_4 + 2\text{KOH} + 3\text{H}_2\text{C}_2\text{O}_4 = \text{K}_2(\text{OsO}_2)(\text{C}_2\text{O}_4)_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}.
\]

Similarly, the action of hydrochloric acid on the tetroxide in the presence of potassium chloride solution leads to the formation of potassium osmyl chloride:

\[
\text{OsO}_4 + 4\text{HCl} + 2\text{KCl} = \text{K}_2(\text{OsO}_2)\text{Cl}_4 + \text{Cl}_2 + 2\text{H}_2\text{O}.
\]

In this case the hydrochloric acid itself acts as the reducing agent, free chlorine being liberated.

It is interesting to note, in passing, that a similar reaction applied to ruthenium tetroxide led Howe (see p. 148) to discover the oxychlororuthenates of caesium and rubidium.

Osmyl sulphites readily lend themselves to preparation in this manner. Rosenheim and Sasserath\(^2\) first prepared sodium osmyl sulphite by passing sulphur dioxide through a solution of osmium tetroxide in caustic soda.

Now in the foregoing reactions the osmium is used in the form of its tetroxide, in which its valency is 8. The first action is that of the reducing agent, which lowers its valency to six. Then comes the formation of the osmyl derivative. For example, the preparation of potassium osmyl oxalate takes place in two stages, namely, (1) the reduction of OsO\(_4\) to OsO\(_2\), which, in the presence of the potassium hydroxide, yields potassium osmate, K\(_2\)OsO\(_4\); and (2) interaction of the last named with 2 molecules of oxalic acid to form the osmyl derivative. These stages may be expressed as follows:

\[
\begin{align*}
(1) & \quad \text{OsO}_4 + \text{H}_2\text{C}_2\text{O}_4 + 2\text{KOH} = \text{K}_2\text{OsO}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O} \\
(2) & \quad \text{K}_2\text{OsO}_4 + 2\text{H}_2\text{C}_2\text{O}_4 = \text{K}_2(\text{OsO}_2)(\text{C}_2\text{O}_4)_2 + 2\text{H}_2\text{O}.
\end{align*}
\]

By starting, therefore, with potassium osmate, in which the osmium is already in the hexavalent condition, the osmyl derivatives may usually be prepared with greater ease, the reaction proceeding according to equation (2) above, or, in general, as follows:

\[
\text{K}_2\text{OsO}_4 + 4\text{HX} = \text{K}_2(\text{OsO}_2)\text{X}_4 + 2\text{H}_2\text{O}.
\]

Osmyl derivatives may change their acid radicles in contact with free acids in the same manner as ordinary salts. For example, just as hydrochloric acid decomposes potassium nitrite with the formation of potassium chloride:

$$\text{KNO}_2 + \text{HCl} = \text{KCl} + \text{HNO}_3,$$

so potassium osmyl nitrite, in the same way, yields potassium osmyl chloride. Thus:

$$\text{K}_2(\text{OsO}_2)(\text{NO}_2)_4 + 4\text{HCl} = \text{K}_2(\text{OsO}_2)\text{Cl}_4 + 4\text{HNO}_2.$$  

Interchange of the negative radicles can also take place between osmyl and neutral salts. Thus the addition of neutral potassium oxalate to a concentrated solution of potassium osmyl chloride yields a precipitate of potassium osmyl oxalate:

$$\text{K}_2(\text{OsO}_2)\text{Cl}_4 + 2\text{K}_2\text{C}_2\text{O}_4 = \text{K}_2(\text{OsO}_2)(\text{C}_2\text{O}_4)_2 + 4\text{KCl}.$$ 

Potassium nitrite, under similar conditions, causes crystals of potassium osmyl nitrite to form. Osmyl derivatives are not stable in neutral aqueous solution, although a small quantity of acid suffices to prevent decomposition. The neutral water decomposes them with the formation of a black precipitate of what has usually been described as osmic acid (see p. 220). Thus, in the case of the chloride:

$$\text{K}_2(\text{OsO}_2)\text{Cl}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{OsO}_4 + 2\text{KCl} + 2\text{HCl}.$$ 

The reaction, however, does not continue to completion, since the free hydrochloric acid formed during the initial stages preserves the remainder from decomposition.

With aqueous potassium hydroxide solution, potassium osmate results. Thus:

$$\text{K}_2(\text{OsO}_2)\text{X}_4 + 4\text{KOH} = \text{K}_2\text{OsO}_4 + 4\text{KX} + 2\text{H}_2\text{O}.$$ 

Boiling with an excess of hydrochloric acid results in the complete displacement of oxygen by chlorine, a chlorosmate or osmichloride being formed:

$$\text{K}_2(\text{OsO}_2)\text{X}_4 + 8\text{HCl} = \text{K}_2\text{OsCl}_6 + 4\text{HX} + \text{Cl}_2 + 2\text{H}_2\text{O}.$$ 

Addition of ammonia to an aqueous solution of an osmyl salt causes the formation of an ammine derivative. Thus:

$$\text{K}_2(\text{OsO}_2)\text{X}_4 + 4\text{NH}_3 = (\text{OsO}_2)(\text{NH}_3)_4\text{X}_2 + 2\text{KX}.$$ 

Of the numerous osmyl derivatives that have been prepared, perhaps the most interesting and important is:

Potassium Osmyl Chloride, $\text{K}_2(\text{OsO}_2)\text{Cl}_4$—This salt is readily prepared by the action of hydrochloric acid upon potassium osmyl nitrite, or upon the oxy-osmyl salt. Thus:

$$\text{K}_2(\text{OsO}_2)\text{O}(\text{NO}_2)_2 + 4\text{HCl} = \text{K}_2(\text{OsO}_2)\text{Cl}_4 + 2\text{HNO}_2 + \text{H}_2\text{O}.$$ 

---

1 In the above cases, of course, the nitrous acid decomposes, yielding oxides of nitrogen but for the sake of clearness this is not represented in the equations.
2 See this Series, Volume X.
* See p. 228.
If a very slight excess of acid is taken, the reaction is quantitative. The action must not be allowed to proceed too energetically, otherwise the chlorosmate is formed (vide supra).

The salt is also obtained by acting on potassium osmate with hydrochloric acid. At first there is precipitated a black powder, usually regarded as osmic acid (but see p. 220). This dissolves entirely in excess of the acid on warming, yielding the osmyl chloride. Thus:

\[ \text{K}_2\text{OsO}_4 + 2\text{HCl} = 2\text{KCl} + \text{H}_2\text{OsO}_4. \]
\[ \text{H}_2\text{OsO}_4 + 2\text{KCl} + 2\text{HCl} = \text{K}_2(\text{OsO}_2\text{Cl})_4 + 2\text{H}_2\text{O}. \]

Although the neutral aqueous solution is not very stable, the contrary is true in the presence of a small quantity of acid.

Cooling of a concentrated, warm solution yields the anhydrous salt, whilst slow cooling causes the dihydrate, \( \text{K}_2(\text{OsO}_2\text{Cl})_4 \cdot 2\text{H}_2\text{O} \), to crystallise out as red octahedra. The last named rapidly lose their water on warming in a current of hydrogen gas.

In the anhydrous condition potassium osmyl chloride also crystallises in red octahedra, which are readily soluble in water. From the solution a black precipitate of osmic acid separates as explained above. When heated in a current of hydrogen the salt is decomposed at 200° C., metallic osmium being obtained.

**Ammonium Osmyl Chloride**, \((\text{NH}_4)_2\text{OsO}_2 \cdot \text{Cl}_4\), obtained by the action of hydrochloric acid upon ammonium osmyl oxy-nitrite, yields red crystals isomorphous with the corresponding potassium salt, than which, however, they are rather less soluble in water.

**Potassium Osmyl Bromide**, \( \text{K}_2(\text{OsO}_2\text{Br})_4 \cdot 2\text{H}_2\text{O} \), has been obtained in the hydrated condition only, and is isomorphous with the corresponding hydrated chloride.\(^1\) **Ammonium Osmyl Bromide**, \((\text{NH}_4)_2\text{OsO}_2 \cdot \text{Br}_4\), has likewise been prepared, but no **Iodo Derivatives** have as yet been isolated.\(^1\)

**Potassium Osmyl Nitrite**, \( \text{K}_2(\text{OsO}_2)(\text{NO}_2)_4 \), results when osmium tetroxide is reduced with nitric oxide in the presence of potassium nitrite: \(^1\)

\[ \text{OsO}_4 + 2\text{NO} + 2\text{KNO}_2 = \text{K}_2(\text{OsO}_2)(\text{NO}_2)_4. \]

It may also be prepared by cooling a warm solution of potassium osmyl chloride, containing a trace of acid, after addition of potassium nitrite in the requisite quantity. Thus:

\[ \text{K}_2(\text{OsO}_2\text{Cl})_4 + 4\text{KNO}_2 = \text{K}_2(\text{OsO}_2)(\text{NO}_2)_4 + 4\text{KCl}. \]

The crystals of potassium osmyl nitrite obtained by cooling of the warm, concentrated solution readily decompose; even in closed tubes, if exposed to sunlight, the decomposition is rapid, needles of osmium tetroxide and brown nitrous fumes appearing:

\[ \text{K}_2(\text{OsO}_2)(\text{NO}_2)_4 = \text{OsO}_4 + 2\text{NO} + 2\text{KNO}_2. \]

The crystals are decomposed by water, but osmic acid is not precipitated owing to oxidation of the osmium to tetroxide by the nitrous acid. With excess of potassium hydroxide potassium osmate is formed:

\[ \text{K}_2(\text{OsO}_2)(\text{NO}_2)_4 + 4\text{KOH} = \text{K}_2\text{OsO}_4 + 4\text{KNO}_2 + 2\text{H}_2\text{O}. \]

If, however, potassium hydroxide is added, little by little, to a solution of the osmyl nitrate in the proportion of two molecules of hydroxide to one of nitrite, a new salt, namely, potassium osmyl oxy-nitrite, is obtained. Thus:

\[ K_2(\text{OsO}_2)\text{(NO}_2)\text{}_4 + 2\text{KOH} = K_2(\text{OsO}_2)\text{O(NO}_2)\text{}_2 + 2\text{KNO}_2 + \text{H}_2\text{O}. \]

Ammonia reacts with an aqueous solution of osmyl nitrite to give an ammino derivative,

\[ \text{OsO}_3(\text{NH}_3)\text{(NO}_2)\text{}_2. \]

Several Osmyl Oxalates have been prepared and described, notably those of potassium, sodium, ammonium, silver, barium, and strontium.

**OSMYL OXY DERIVATIVES**

Osmyl oxy derivatives differ from osmyl salts in that they contain an additional atom of oxygen, but have two monovalent negative radicles the fewer. The general formula for these substances is thus:

\[ M_2(\text{OsO}_3)X\text{a}, \]

where M and X have the same significance as hitherto (see p. 223).

Osmyl oxy salts have been made the subject of careful study by Wintrebert. They can frequently be prepared by the action of an oxidizable salt upon osmium tetroxide. Thus, potassium nitrite reacts with the tetroxide as follows:

\[ \text{OsO}_4 + 3\text{KNO}_2 = K_2(\text{OsO}_3)(\text{NO}_2)\text{}_2 + \text{KNO}_3. \]

Potassium oxalate reacts in a similar manner, but more slowly, whilst ammonium oxalate yields an ammino salt, namely:

\[ \text{OsO}_2(\text{NH}_3)\text{C}_2\text{O}_4. \]

Having once obtained a suitable osmyl oxy salt such as potassium or sodium osmyl oxynitrite by a method similar to the above, it is not difficult by suitably choosing the reagents to prepare many other derivatives. Thus, the ammonium salt may readily be obtained by double decomposition of ammonium chloride and the sodium salt. Thus:

\[ \text{Na}_2(\text{OsO}_3)(\text{NO}_2)\text{}_2 + 2\text{NH}_4\text{Cl} = (\text{NH}_4)\text{2OsO}_3(\text{NO}_2)\text{}_2 + 2\text{NaCl}. \]

Again, by acting on this new salt with hydrochloric acid in the cold, ammonium osmyl oxychloride is produced:

\[ (\text{NH}_4)\text{2OsO}_3(\text{NO}_2)\text{}_2 + 2\text{HCl} = (\text{NH}_4)\text{2OsO}_3\text{Cl}_2 + 2\text{HNO}_2. \]

When, therefore, any particular derivative is difficult to prepare by the direct method, it is frequently possible to apply indirect methods with success.

Osmyl oxy salts exhibit practically the same properties as osmyl

---

1 See p. 231.
3 Potassium salts apparently do not behave in this way with halogen acids, but are converted directly into osmyl derivatives; *vide infra*. If the above reaction is carried out in the warm, the ammonium salt is converted into the osmyl chloride or even to chlorosmate, (NH₄)₂OsCl₄. See p. 227.
derivatives. For example, water decomposes them with formation of osmic acid:

\[ \text{M}_2(\text{OsO}_3)\text{X}_2 + \text{H}_2\text{O} = \text{H}_2\text{OsO}_4 + 2\text{MX}. \]

The reaction, which proceeds slowly in the cold, is rapid on warming. Potassium hydroxide reacts similarly. Thus:

\[ \text{M}_2(\text{OsO}_3)\text{X}_2 + 2\text{KOH} = \text{K}_2\text{OsO}_4 + 2\text{MX} + \text{H}_2\text{O}, \]

whilst the halogen acids yield halogen osmates. Thus, in the case of hydrochloric acid:

\[ \text{M}_2(\text{OsO}_3)\text{Cl}_2 + 6\text{HCl} = \text{M}_2\text{OsCl}_6 + \text{Cl}_2 + 3\text{H}_2\text{O}. \]

Osmyl oxy salts may frequently be converted into osmyl derivatives by the action of a reducing acid. For example, ammonium osmyl oxalate is reduced by oxalic acid to ammonium osmyl oxalate as follows:

\[ (\text{NH}_4)_2\text{OsO}_3.\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4 = (\text{NH}_4)_2\text{OsO}_2(\text{C}_2\text{O}_4)_2 + \text{H}_2\text{O}. \]

In a similar manner it is possible to convert an osmyl oxy derivative containing a certain acid radicle into an osmyl salt with another acid radicle. Thus potassium osmyl oxynitrite with hydrochloric acid yields potassium osmyl chloride:

\[ \text{K}_2\text{OsO}_3(\text{NO}_2)_2 + 4\text{HCl} = \text{K}_2(\text{OsO}_2)\text{Cl}_4 + 2\text{HNO}_2 + \text{H}_2\text{O}. \]

Transformation in the opposite direction, namely, from osmyl to osmyl oxy derivatives, is more difficult to effect, although it has been accomplished in the preparation of potassium osmyl oxynitrite (see p. 228).

**Ammonium Osmyl Oxychloride**, \((\text{NH}_4)_2\text{OsO}_3.\text{Cl}_2\), is obtained by careful addition of hydrochloric acid to the corresponding nitrite:

\[ (\text{NH}_4)_2\text{OsO}_3(\text{NO}_2)_2 + 2\text{HCl} = (\text{NH}_4)_2\text{OsO}_3\text{Cl}_2 + 2\text{HNO}_2. \]

It is an advantage to use a slight excess of acid, as it tends to prevent oxidation from the nitrous fumes. The temperature, however, must not be greatly raised, otherwise the osmyl salt, \((\text{NH}_4)_2\text{OsO}_2.\text{Cl}_2\), or even the chlorosmate, \((\text{NH}_4)_2\text{OsCl}_4\), may result. On very gently warming the nitrous fumes are disengaged, and a yellow crystalline deposit of ammonium osmyl oxychloride is obtained, which is but slightly soluble in water. With caustic potash, ammonia and potassium osmate are formed, the latter imparting to the solution its characteristic red-violet colour.

**Potassium Osmyl Oxychloride** is apparently too unstable to exist, since its osmyl oxynitrite is converted directly into osmyl chloride by the action of hydrochloric acid.

**Ammonium Osmyl Oxybromide**, \((\text{NH}_4)_2\text{OsO}_3\text{Br}_2\), is prepared in an analogous way to the chloride. Thus:

\[ (\text{NH}_4)_2\text{OsO}_3(\text{NO}_2)_2 + 2\text{HBr} = (\text{NH}_4)_2\text{OsO}_3\text{Br}_2 + 2\text{HNO}_2. \]

The salt is obtained as a yellow, crystalline powder, but slightly soluble in water. With potassium hydroxide ammonia is evolved, potassium osmate remaining, thus indicating the hexavalent nature of the osmium.

No corresponding potassium salt is known.

Potassium Osmyl Oxynitrite, \(K_2(\text{OsO}_3)(\text{NO}_2)_2\).SH_2 > is readily obtained \(1\) as the result of the direct action of a concentrated solution of potassium nitrite on osmium tetroxide:

\[
\text{OsO}_4 + 3\text{KNO}_2 = K_2(\text{OsO}_3)(\text{NO}_2)_2 + \text{KNO}_3.
\]

If nitric oxide is passed through a solution of osmium tetroxide in potassium hydroxide containing exactly one molecule of the former to two of the latter, potassium osmyl oxynitrite is formed, and may be isolated on concentration of the solution. The reaction probably proceeds as follows:

\[
\text{OsO}_4 + 2\text{KOH} + 2\text{NO} = \text{H}_2\text{OsO}_4 + 2\text{KNO}_2
\]

\[
2\text{KNO}_2 + \text{H}_2\text{OsO}_4 = \text{K}_2(\text{OsO}_3)(\text{NO}_2)_2 + \text{H}_2\text{O}.
\]

An interesting method of preparing the osmyl oxynitrite consists in acting on the osmyl derivative with potassium hydroxide. Thus:

\[
\text{K}_2(\text{OsO}_3)(\text{NO}_2)_2 + 2\text{KOH} = \text{K}_2(\text{OsO}_3)(\text{NO}_2)_2 + \text{H}_2\text{O} + 2\text{KNO}_2.
\]

This is one of the few cases in which it is possible to pass from an osmyl salt to an osmyl oxy salt.

Potassium osmyl oxynitrite crystallises in the form of brownish black needles, which dissolve in aqueous potash, yielding potassium osmate. The crystals are only slightly soluble in cold water. At 85° C. they begin to lose their water of crystallisation and acquire a yellowish tint. When crushed in a mortar the odours of osmium tetroxide and nitrogen peroxide become apparent. When heated in a current of hydrogen to 200° C. the salt decomposes without explosion, free osmium remaining behind.

Sodium Osmyl Oxynitrite, \(\text{Na}_2(\text{OsO}_3)(\text{NO}_2)_2\), is apparently formed by the action of sodium nitrite on osmium tetroxide.\(1\) It has not been isolated from the resulting solution, as evaporation yields merely a syrupy liquid. Addition of ammonium chloride to the solution changes its colour from deep brown to yellow, and a yellow crystalline powder, namely, Ammonium Osmyl Oxynitrite, \((\text{NH}_4)_2\text{OsO}_3(\text{NO}_2)_2\), is deposited.

The corresponding silver, barium, and strontium salts have been prepared, crystallising with one, four, and three molecules of water respectively.\(1\) The osmyl oxyoxalates of potassium and ammonium have also been prepared.

OSMIUM AND SULPHUR

Osmium Disulphide, \(\text{Os}_2\text{S}_2\), results \(2\) when a current of hydrogen sulphide is passed over dry osmium oxysulphide \((\text{vide infra})\), which is gently warmed. At higher temperatures the reaction is very vigorous, the whole mass glowing with heat:

\[
\text{Os}_2\text{O}_3(\text{SH})_2 + 2\text{H}_2\text{S} = 2\text{OsS}_2 + 3\text{H}_2\text{O}.
\]

It is also produced on passing hydrogen sulphide through a neutral solution of an alkali osmate \(3\) or chlorosmate.\(4\)

---

Osmium Tetrasulphide, $\text{OsS}_4$, is obtained as a brown precipitate when hydrogen sulphide is passed through an acidified aqueous solution of the tetroxide.\(^1\) It is not affected by solutions of the hydroxides or sulphides of the alkali metals, in which it is insoluble.\(^2\) It oxidises readily in the air, and at high temperatures it decomposes, yielding the free metal. When gently heated in vacuo it is stated to yield a sulphide of composition $^3 \text{Os}_2\text{S}_5$.

**Osmium Oxysulphide**, $\text{Os}_2\text{O}_3(\text{SH})_2$, is obtained as a brown powder by the action of hydrogen sulphide on dry osmic acid, $\text{H}_2\text{OsO}_4$. The reaction is very vigorous, the mass being raised to glowing temperature, water and sulphur vapour being emitted:

$$2\text{H}_2\text{OsO}_4 + 4\text{H}_2\text{S} = \text{Os}_2\text{O}_3(\text{SH})_2 + 5\text{H}_2\text{O} + 2\text{S}.$$  

The oxysulphide dissolves in acids evolving hydrogen sulphide. The heat of the reaction indicates that water cannot be present as such in the sulphide. Morah and Wischin suggest the following constitution:

$$\begin{align*} \text{SH} \\ \text{Os=O} \\ \text{O} \\ \text{Os=O} \\ \text{SH} \end{align*}$$

This is supported to some extent by the facts that (1) the oxysulphide dissolves in sodium carbonate solution with evolution of carbon dioxide, and (2) yields with solid potassium sulphide a yellow substance, hydrogen sulphide escaping. These facts suggest that the oxysulphide has a distinctly acid nature. Again, with ethyl iodide, mercaptan is produced. This clearly indicates the presence of an $\text{SH}$ group. Thus:

$$\begin{align*} \text{SH} \\ \text{Os=O} \\ \text{O} \\ \text{Os=O} \\ \text{SH} + 2\text{C}_2\text{H}_5\text{I} & \rightarrow \text{O} \\ & +2\text{HI} \rightarrow 2\text{C}_2\text{H}_5\text{SH} + 2\text{OsO}_2 \\ \text{OS=O} \\ \text{OS=O} \end{align*}$$

The precipitated osmium dioxide discloses its unsaturated nature by exploding when heated with organic substances. E. von Meyer\(^5\) describes the preparation of an osmium oxysulphide by passage of hydrogen sulphide through a solution of osmium tetroxide.

**Osmium Sulphite, $\text{OsSO}_3$**—This salt is prepared by reduction of a solution of osmium tetroxide with sulphur dioxide.\(^6\) The solution at first becomes yellow, and finally assumes an indigo-blue colour. On

---

evaporating to dryness and drying at 100° C. in vacuo the salt is obtained as a black, insoluble powder, which, however, dissolves in acid.  

**Complex Osmisulphites.** On passing sulphur dioxide through an alkaline solution of osmium tetroxide in potassium hydroxide until it becomes almost neutral, a brown crystalline precipitate is obtained, namely, the complex sodium osmisulphite, \(3\text{Na}_2\text{O} \cdot \text{OsO}_3 \cdot 4\text{SO}_2 + 5\text{H}_2\text{O}\), or:

\[
\text{Na}_2\text{O} \cdot \text{Os} \equiv (\text{SO}_3\text{Na})_4 + 5\text{H}_2\text{O}.
\]

The salt dissolves easily in warm water, yielding a reddish brown solution. On treatment with caustic soda, a violet solution of sodium osmate is obtained, whilst barium chloride and silver nitrate precipitate respectively a light brown barium salt and a yellowish brown silver salt. By treatment of osmium tetroxide in potassium hydroxide under similar conditions with sulphur dioxide the complex \(7\text{K}_2\text{O} \cdot 4\text{OsO}_3 \cdot 10\text{SO}_2\) has been obtained both in the anhydrous condition and with 3 and 7 molecules of water respectively.

In concentrated alkaline solution, prolonged action of sulphur dioxide yields the complex \(11\text{K}_2\text{O} \cdot 4\text{OsO}_3 \cdot 14\text{SO}_2 + 7\text{H}_2\text{O}\).

Both of these salts, on treatment with caustic potash, decompose quantitatively into potassium osmate and sulphite.

By the action of sodium hydrogen sulphite solution on one of sodium chlorosmate at the boiling-point, a whitish brown crystalline compound is obtained, to which the formula

\[
[\text{Os}(\text{SO}_3)_5]\text{Na}_8 \cdot 8\text{H}_2\text{O}
\]

is given.

If, however, an excess of sulphite solution is used, and the mixture allowed to stand for several weeks, needle-shaped crystals of sodium chlorosmisulphite separate out, ranging in colour from dark yellow to bright brown, and containing two atoms of chlorine, thus:

\[
\left[\text{Os}\left(\text{SO}_3\right)_4\right]\text{Na}_6 \cdot 10\text{H}_2\text{O}.
\]

The same salt is also formed by mixing solutions of normal sodium sulphite and chlorosmate in the cold. If, however, the solution is gently warmed, the monochlor derivative,

\[
\left[\text{Os}\left(\text{SO}_3\right)_5\right]\text{Na}_7 \cdot 6\text{H}_2\text{O},
\]

is produced.

**Potassium Hydrogen Chlorosmisulphite**, \(\text{OsCl}_4(\text{SO}_3)_4\text{K}_6\text{H}_2\), obtained by the prolonged action of potassium hydrogen sulphite on potassium osmichloride, crystallises in dark red, monoclinic prisms. When heated with hydrochloric acid it evolves sulphur dioxide, and is converted into potassium osmichloride.

Other complex derivatives have been prepared.

OSMIUM AND SELENIUM

Osmium selenate is not known. In the cold, selenic acid is without action on osmium, but at about 120° C. the metal dissolves, yielding a colourless solution which contains selenious acid and osmium tetroxide.1

OSMIUM AND NITROGEN

**Osmium Di-ammine Hydroxide**, OsO(NH₂)₂(OH)₂, results when the tetroxide is dissolved in concentrated aqueous ammonia and heated in a closed vessel to 50° C. On opening the vessel and evaporating the excess of ammonia, osmosammine hydroxide is obtained as a dark brown powder.2 It unites with acids to form salts, and upon being heated readily decomposes. When boiled with alkalies ammonia is evolved and hydrated osmium dioxide remains.3

The most important salt is the chloride, which yields brown crystals which are decomposed by water, giving a basic salt.

- **Osmyl Tetra-ammine Hydroxide**, OsO₂(NH₂)₄(OH)₂, is obtained by double decomposition of its sulphate with barium hydroxide,4 or of its chloride with moist silver oxide.5 The solution is not stable, and on concentration ammonia is evolved. The most important salt of this base is

**Osmyl Tetra-ammine Chloride**, OsO₂(NH₂)₄Cl₂, and is obtained as a yellow, crystalline precipitate when ammonium chloride is added to aqueous potassium osmate.6 It is but slightly soluble in water, and boiling water decomposes it into osmium tetroxide and osmium di-ammine hydroxide. Its solution gives a violet coloration with potassium ferrocyanide, a reaction that may be utilised for the detection of osmium.7 It is insoluble in alcohol and in hydrochloric acid. When heated it decomposes completely, yielding a mass of spongy osmium.

The corresponding nitrate and sulphate are known.

**Osmiamic Acid**, OsNO₂H, may be prepared by decomposing the barium salt with dilute sulphuric acid, or the silver salt with hydrochloric acid. The dilute aqueous solution thus obtained is fairly stable, but upon concentration it decomposes.

Joly8 suggested that osmiamic acid might well be represented as a nitroso compound by the formula OsO(NO)OH, derived from the unknown trihydroxy compound, Os(NO)(OH)₃, which corresponds to Ru(NO)(OH)₃.

Such a constitution is in harmony with certain reactions of, for example, its potassium salt, OsNO₂K.9 Thus10 reduction of the last

---

4 Claus, *loc. cit.*
5 Claus, *opus cit.*, 1860, 4, 121.
9 Fritzseche and Struve, who first prepared the potassium salt, suggested for it the formula K₂N₂O₃O₄. Gerhardt (*J. Pharm.*, [iii], 12, 304) showed that this could not be correct. The formula OsNO₂K is due to Joly (*loc. cit.*). Hence the formula for the acid.
named with acidulated stannous chloride yields the amide of potassium chlorosmate, namely, $K_2Os(NH_2)Cl_5$, the supposition being that the $NH_2$ group is formed by direct reduction of an NO group.

Werner and Dinklage, however, have pointed out that cooled hydrochloric acid reacts with potassium osmic acid, evolving chlorine and yielding a well-crystallised salt of composition $K_2OsNCl_5$. This is confirmed by Wintrebert. Now Werner and Dinklage regard it as improbable that a nitroso group can be present in the original acid, and suggest the formula:

$$\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{NH}
\end{array}$$

the imido group replacing one atom of oxygen in the tetroxide.

To the potassium salt they give the tautomeric formula:

$$\begin{array}{c}
\text{O} \\
\text{Os} \\
\text{K} \\
\text{O}
\end{array}$$

**Potassium Osmimamate**, $OsNO_3K$, may be obtained by the action of ammonia on a cold solution of osmium tetroxide in potassium hydroxide. Thus:

$$OsO_4 + KOH + NH_3 = OsNO_3K + 2H_2O.$$  

The salt crystallises in orange-yellow, tetragonal pyramids, which partially decompose upon recrystallisation, becoming darker in colour. When heated, nitrogen gas is evolved.

The corresponding barium, silver, and sodium salts have been prepared.

**Potassium Nitrosoclorosmate**, $K_2Os(NO)Cl_5$, may be readily obtained by boiling potassium osminitrite with concentrated hydrochloric acid:

$$2K_2Os(NO_2)Cl_5 + 10HCl = 2K_2Os(NO)Cl_5 + 3NO + 5NO_2 + 5H_2O.$$  

The salt yields orthorhombic crystals isomorphous with the corresponding nitrosochlor-ruthenate (see p. 150). It is very stable for a compound of osmium. Its aqueous solution is quite stable, and even nitric acid does not attack the salt as vigorously as usual.

**Potassium Nitrosobromosmate**, $K_2Os(NO)Br_5$, and **Potassium Nitroso-iodosmate**, $K_2Os(NO)I_5$, are prepared in a similar manner to the chloro derivative, with which they are isomorphous.

**Osmium Nitrite**, $Os(NO_2)_3$, is obtained when barium osminitrite is decomposed with the theoretical amount of dilute sulphuric acid. By operating in the cold the evolution of nitrous fumes may be avoided, and the liquid appears to contain osminitrous acid, $H_2Os(NO_2)_5$. On concentrating, nitrous fumes are evolved, and osmium nitrite is obtained as a deep brown powder, stable in air.

---

OSMIUM AND ITS COMPOUNDS

Potassium Osminitrite, \( \text{K}_2\text{Os(NO}_2\text{)}_5 \), is obtained \(^1\) by the action of excess of potassium nitrite on a solution of potassium chlorosmate at a temperature of about 80° C.\(^2\):

\[
\text{K}_2\text{OsCl}_6 + 7\text{KNO}_2 = \text{K}_2\text{Os(NO}_2\text{)}_5 + 6\text{KCl} + \text{KNO}_3 + \text{NO}.
\]

It is necessary to carry out the operation away from air, as otherwise large quantities of osmyl oxynitrite (see p. 228) are formed.

The crystals obtained are flattened parallelopipeds, canary yellow in colour, and readily soluble in water.\(^3\)

Sodium Osminitrite, \( \text{Na}_2\text{Os(NO}_2\text{)}_5 \cdot 2\text{H}_2\text{O} \), may be obtained advantageously by double decomposition with the silver or barium salt.\(^3\) Its crystals are a little more soluble in water than those of the potassium salt, and are possessed of an orange-yellow colour.

Ammonium Osminitrite, \( (\text{NH}_4)_2\text{Os(NO}_2\text{)}_5 \), may be prepared in the same manner as the sodium salt. It yields orange-yellow crystals which are stable in dry air.

Barium Osminitrite, \( \text{BaOs(NO}_2\text{)}_5 \cdot \text{H}_2\text{O} \), is obtained by the action of barium chloride on a hot aqueous solution of potassium osminitrite and crystallising at temperatures above 15° C. It yields yellow plates.

At temperatures below 15° C. the salt separates out as amber-yellow needles containing four molecules of water.

Osminitrites of silver (golden yellow), strontium (orange), calcium (orange-yellow), magnesium (sulphur-yellow), and zinc (orange-yellow) have been prepared.\(^3\)

Osmium Cyanide, \( \text{Os(CN)}_2 \).—When an alkali osmocyanide is warmed with concentrated hydrochloric acid, hydrogen cyanide is gradually evolved, and osmium cyanide forms as a dark violet precipitate \(^4\):

\[
4\text{MCN} \cdot \text{Os(CN)}_2 + 2\text{HCl} = \text{OsCN} + 2\text{MCl} + 2\text{HCN}.
\]

Hydrogen Osmocyanide, Osmocyanic Acid, \( \text{H}_4\text{Os(CN)}_6 \), is best prepared by adding concentrated hydrochloric acid to a cold, saturated solution of potassium osmocyanide. On standing, osmocyanic acid separates out in small white scales. These are washed with concentrated hydrochloric acid, dissolved in alcohol, and finally precipitated out with ether, as brilliant crystals.\(^5\)

Obtained in this way osmocyanic acid is anhydrous, and stable in dry air. In moist air it gives a blue colour, probably owing to the formation of osmium cyanide. It readily dissolves in water, giving an acid reaction. It is also soluble in alcohol, but not in ether. It has an astringent, metallic taste. Analysis agrees with the formula given above.\(^6\) It unites with bases to form salts known as osmocyanides, which closely resemble the corresponding ferro- and rutheno-cyanides.

Potassium Osmocyanide, \( \text{K}_2\text{Os(CN)}_6 \cdot 3\text{H}_2\text{O} \), is obtained on heating to fusion ammonium chlorosmate with one and a half times its weight

\(^1\) Gibbs, Amer. J. Sci., 1862, 34, 344.
\(^3\) Wintrebert, Compt. rend., 1905, 140, 555.
\(^5\) Martinus, opus cit., p. 15.
\(^6\) Martinus, opus cit.; Claus (Beiträge, etc., 1854, p. 99), who first prepared this acid in an analogous manner to that described by Martinus, did not analyse it; he concluded that its formula must be as above on the ground of its close resemblance to the corresponding ruthenium compound.
of potassium cyanide¹ for ten to fifteen minutes. Extraction of the melt with boiling water, and subsequent evaporation, yields crystals of potassium osmocyanide containing three molecules of water.

Martius² recommended the following method: Osmium tetroxide is dissolved in potassium hydroxide solution, the latter being present in sufficient quantity to render the whole distinctly alkaline. The dark, reddish brown solution is now mixed with the requisite quantity of potassium cyanide, whereby the colour becomes increasingly darker, until finally it is greenish black. On complete evaporation and gentle warming, the dry residue gradually changes in colour through yellow to white. This product is redissolved, and from the solution crystals are obtainable in the usual way.

Potassium osmocyanide is easily soluble in hot water, and the boiling saturated solution deposits, on cooling, the salt as a fine yellow powder. It is almost insoluble in alcohol, and quite insoluble in ether. On slow evaporation of its aqueous solution, the salt yields crystalline leaflets isomorphous with the ferro- and rutheno-cyanides of potassium.³ It is a useful reagent for detecting iron, giving with ferrous salts a violet precipitate, and with ferric salts a dark violet-blue precipitate.⁴

Anhydrous potassium osmocyanide is white, and when heated to redness in the absence of air yields some free osmium, whilst in air osmic acid is formed. With concentrated hydrochloric acid, hydrogen osmocyanide is formed (vide supra). Soon, however, a further reaction sets in whereby hydrogen cyanide is evolved and osmium cyanide is precipitated out. Other mineral acids behave similarly.

When chlorine is passed through a solution of potassium osmocyanide, the latter assumes a dark colour like that of potassium ferrocyanide. Martius⁵ could not obtain any osmocyanide, however, on evaporation, but found that, on standing, potassium chlorosmate was formed.

Barium Osmocyanide, $\text{Ba}_2\text{Os(CN)}_6 \cdot 6\text{H}_2\text{O}$, is obtained by adding an excess of baryta water to the violet precipitate resulting from interaction of a ferric salt with potassium osmocyanide. The ferric osmocyanide is at once decomposed, yielding a brown precipitate of ferric hydroxide, whilst barium osmocyanide passes into solution,⁶ imparting to it a yellow colour. Any excess of barium hydroxide is removed by passing carbon dioxide through, and on slow evaporation of the filtered liquid the salt crystallises out in stable, reddish yellow crystals, readily soluble in water and aqueous alcohol. On heating to 50–60° C. the whole of the water of crystallisation is expelled, the anhydrous salt remaining as a yellow powder.

Barium Potassium Osmocyanide, $\text{BaK}_2\text{Os(CN)}_6 \cdot 3\text{H}_2\text{O}$, has also been prepared (Martius).

Detection and Estimation of Osmium.—See Chapter X.

¹ Claus, opus cit., p. 98.
² Martius, opus cit., 1854, p. 17.
³ Dufet, Compt. rend., 1866, 120, 377.
⁴ Claus, opus cit.
⁵ Martius, opus cit., p. 21.
⁶ Martius, opus cit., p. 22.
Occurrence and History.—Iridium is found in nature alloyed with platinum or other allied metals, particularly in platiniridium and osmiridium (see analyses, pp. 208, 258). Nevanskite, a variety of osmiridium, contains over 40 per cent. of iridium, whilst siserskite, another variety, contains up to 30 per cent. of the same metal. Iridium was first identified as a new metal by Tennant in 1804, who suggested its name in recognition of the different colours exhibited by its salts. Iridium has been detected in meteoric iron, and its presence in the photosphere of the sun has been demonstrated spectroscopically. The world’s annual production of iridium in normal times probably does not exceed 5000 oz.

Preparation.—Iridium may be conveniently prepared from osmiridium. This alloy is fused in turn with zinc, and then with barium dioxide and nitrate. The residue, after treatment with acid and removal of osmium by distillation, consists of iridium and a small quantity of ruthenium, as explained on page 136. The liquid is reduced to small bulk, ammonium chloride and a little nitric acid added, and the whole taken to dryness on the water-bath. A violet-black crystalline residue is obtained, consisting mainly of ammonium chloriridate. This is washed with semi-saturated ammonium chloride solution until the washings are colourless, dried, and heated to redness, a current of hydrogen being finally passed over to remove the last traces of chlorine and oxygen. On cooling, the metallic residue, consisting mainly of iridium with a little ruthenium, is treated with aqua regia, which removes a little platinum and osmium. Fusion with potassium nitrate and hydroxide and subsequent washing removes any ruthenium as soluble potassium ruthenate, the insoluble residue being finally heated to whiteness until every trace of osmium has been volatilised. The residue gradually melts to a button of fairly pure iridium.

Purification of Iridium.—In practice the purest iridium obtained by the foregoing process invariably contains small quantities of platinum, rhodium, ruthenium, and iron. In order to remove these, Matthey treats the metal as follows. The iridium, in a fine state of division, is fused with ten times its weight of lead, and kept in the molten condition

2 Tennant, *Phil. Trans.*, 1804, p. 411.
for some hours. On cooling, the lead is removed with nitric acid, and the residue subjected to prolonged digestion in aqua regia, whereby the platinum is removed, and a mass of iridium, with small quantities of rhodium, ruthenium, and iron, results.

This is fused with potassium hydrogen sulphate at a high temperature, which treatment removes practically all the rhodium, any remaining traces being taken out with the iron at a later stage.

The resulting iridium is fused with ten times its weight of potassium hydroxide and three times its weight of potassium nitrate in a gold crucible. This operation takes a considerable time, the iron being oxidised, the iridium converted into insoluble potassium iridate, and the ruthenium to soluble potassium ruthenate.

The whole is extracted with water, and the precipitate washed with water containing alkaline sodium hypochlorite in solution, until the washings are no longer coloured, signifying the removal of most of the ruthenium. The residue, consisting mainly of blue oxide of iridium, is now allowed to remain for a time suspended in a cold solution of sodium hypochlorite, after which it is gradually raised to the boiling-point and heated until the distillate no longer reddens a solution of hydrochloric acid in diluted alcohol. The residue is again heated with potassium nitrate and alkaline sodium hypochlorite solution charged with chlorine, until the last trace of ruthenium has disappeared.

It now remains to remove the iron and traces of rhodium. This is effected by dissolving in aqua regia, evaporating to dryness, and redissolving in water. After filtering, the dark-coloured solution is slowly poured into a concentrated solution of sodium hydroxide containing sodium hypochlorite, and should remain clear without any perceptible precipitate. The solution is now distilled, and chlorine gas passed through; the distillate on being collected in a solution of hydrochloric acid in dilute alcohol should yield no coloration, showing that ruthenium is entirely absent. The chlorine precipitates out the greater part of the iridium as blue oxide, which is washed and dried and reduced by ignition in a porcelain tube in a current of carbon monoxide mixed with dioxide, as obtained by the action of sulphuric acid upon oxalic.

Metallic iridium is thus obtained together with oxide of iron. The whole is heated to redness with potassium hydrogen sulphate, which removes the iron and any remaining traces of rhodium. The residue is well washed with water, then with chlorine water to remove any traces of gold, and finally with hydrochloric acid to take out any silica which may have accidentally been introduced with the alkalies or have come from the vessels employed. The resulting iridium is calcined with charcoal and melted into an ingot.

Matthé states that the metal prepared in this manner, even with the utmost care, will still contain very minute, though almost inappreciable, traces of oxygen, ruthenium, rhodium, and possibly iron.

Leidie recommends the following method of purifying iridium as obtained by the process just described. The metal in a fine state of division is heated to dull redness with twice its weight of fused sodium chloride in a current of dry chlorine. On cooling, the mass is extracted with water containing a little hydrochloric acid. The solution is filtered, raised to 50° C., and sodium nitrite added until nitrous fumes cease to be evolved. Sufficient sodium carbonate

1 Leidie, Compt. rend., 1899, 129, 214.
is now introduced to render the solution decidedly alkaline, then a slight excess of sodium nitrite, and the whole raised to boiling. The precipitate obtained contains any iron, lead, and gold originally present, whilst in solution are present iridium, together with any ruthenium, rhodium, and osmium, in the form of the following compounds:

- Iridium as Ir₂(NO₂)₆·6NaNO₂
- Ruthenium as Ru₂(NO₂)₆·4NaNO₂
- Rhodium as Rh₂(NO₂)₆·6NaNO₂
- Osmium as Na₂OsO₄

The ruthenium and osmium are best removed by conversion into their volatile oxides, RuO₂ and OsO₄. This is effected by addition of excess of sodium hydroxide to the solution, and passing in chlorine whereby hypochlorites are produced. On continuing to pass in chlorine and gradually raising the temperature, the tetroxides of ruthenium and osmium volatilise, and may be condensed in a cooled receiver. The iridium and rhodium remain behind in solution as double chlorides, namely, sodium chloriridate, Na₂IrCl₆, and sodium chlor-rhodite, Na₃RhCl₄, which are obtained, together with excess of sodium chloride, on evaporating to dryness. The crystalline mass is dissolved in chlorine water and recrystallised, whereby the excess of sodium chloride is removed, the pure double salts separating out. These are dried and heated to 440° C. in a current of dry chlorine, cooled and extracted with chlorine water. The rhodium salt has been converted by this treatment into the insoluble trichloride and remains behind, the sodium chloriridate passing into solution. Addition to the last named of excess of ammonium chloride causes the precipitation of ammonium chloriridate, (NH₄)₂IrCl₆. This is washed in a concentrated solution of ammonium chloride, in which it is insoluble, dried, and reduced at red heat in a current of pure, dry hydrogen. On cooling, the hydrogen is replaced by carbon dioxide, pure iridium remaining.

Antony ¹ prepares pure iridium by precipitation from an acidulated solution of the chloride with metallic zinc. The precipitated metal is treated with nitric acid (density 1·85) containing nitrous acid, whereby osmium and palladium are removed. Repeated extraction with dilute aqua regia (3 parts HCl, 3 parts H₂O, and 1 part HNO₃) dissolves out the bulk of the platinum and any traces of osmium and palladium still remaining.

The metal is now fused with potassium hydrogen sulphate whereby soluble rhodium compound is produced, and the insoluble residue of iridium sesquioxide, Ir₂O₃, is reduced in a current of hydrogen, and converted into potassium chloriridate by heating with potassium chloride in a current of chlorine. Repeated crystallisation to remove any chlor-ruthenate yields the purer salt, still contaminated, however, with traces of platinum. These are removed by reducing the salt to the metallic condition and heating in a current of chlorine and carbon monoxide to 250° C., whereby the platinum volatilises, leaving a dark green mass of iridium, containing a little chloride. The pure metal is readily obtained from this by reduction.

**Physical Properties.**—Native iridium has been found crystallised as cubes, and is stated to occur less frequently as rhombohedra. In an

¹ Antony, *Gazzetta*, 1892, 22, i, 275.
examination of a pure preparation belonging to Stas, Printz could find no evidence of dimorphism or of hexagonal (rhombohedral) crystals. Iridium is a hard, brittle metal, which can be filed and which takes a polish. In appearance it lies between silver and tin; it is not ductile, however, even at red heat. Its specific heat is 0.0823, and its coefficient of linear expansion with rise of temperature (0–80°C) is 0.000,007. The density of the native metal is 22.6 to 22.8. For the pure cast metal the value 22.12 has been found. It melts at 2290°C and distils in the electric furnace, its boiling-point being approximately 2550°C. Its vapour, on cooling, is deposited as small crystals.

Liquid iridium dissolves carbon, but liberates it, on cooling, in the form of graphite.

Absorption of Hydrogen.—Iridium foil, when subjected to prolonged cathodic pulverisation in vacuo, becomes capable of absorbing some 800 times its volume of hydrogen at ordinary temperature. The metal becomes considerably altered in appearance, turning dull grey and brittle. Iridium which has been treated in this way yields an amalgam with mercury which is completely soluble in aqua regia; furthermore the iridium becomes capable of exploding electrolytic gas.

The most intense lines in the spectrum are as follow:

```
```

Iridium Black consists of an indefinite mixture of finely divided iridium and its oxides, and is obtained by reducing iridium compounds. For example, the sesquioxide dissolved in alkaline solutions yields a deposit of iridium black on boiling with alcohol, the latter being oxidised to formic acid and aldehyde.

Iridium black is soluble in aqua regia, and like its platinum analogue possesses considerable catalytic activity. For example, it converts ozone into oxygen, hypochlorites into chlorides, and free oxygen and chlorine water into hydrochloric acid and oxygen.

Colloidal Iridium is readily obtained by reducing an aqueous solution of the chloride with hydrazine hydrate or sodium amalgam, in the

6. Deville and Debrey, Compt. rend., 1875, 81, 830.
7. Mendehall and Ingersoll, Phys. Review, 1907, 25, 1. Earlier figures are 2200–2300° (Weyde, Ber., 1879, 12, 440) and 1900° (Viöle, loc. cit.)
9. Moissan, ibid., 1896, 123, 16.
11. Exner and Haschek, Die Spektren der Elemente bei normalem Druck (Leipzig and Wien, 1911).
15. Paal and Amberger, Ber., 1904, 37, 124.
presence of a protective colloid such as gum acacia, or sodium protalbate (or lysalte). Hydrogen, sodium formate, or formaldehyde may also be used, instead of the hydrazine, as reducing agents.¹

When evaporated to dryness over concentrated sulphuric acid in vacuo the solid hydrosol is obtained. This dissolves in warm water, yielding the colloidal solution again. The solution, when shaken with barium sulphate or animal charcoal, is decomposed, the metal being coagulated and thrown out as a precipitate.

Colloidal iridium may also be prepared by Bredig’s method, which consists in sparking between iridium electrodes immersed in ice-cooled water. A current of 20 to 25 amperes at 220 volts gives satisfactory results.² The colour of the hydrosol ranges from red to black, according to the method of preparation. A small current favours the formation of the black solution.

Colloidal iridium readily decomposes hydrogen peroxide solution, the reaction being, as with platinum, mono-molecular; the rate of decomposition is approximately proportional to the concentration of catalyst. Alkali does not affect the reaction velocity, but dilute acids accelerate it. Hydrogen sulphide, mercuric chloride, and certain other substances act as poisons.³ Colloidal iridium is less active, however, than platinum.

Carbon monoxide combines with oxygen, yielding the dioxide at ordinary temperatures when shaken with the hydrosol of iridium.⁴

**Explosive Iridium** is obtained by dissolving an alloy of the metal with excess of zinc in hydrochloric acid, the zinc passing into solution, leaving metallic iridium in a finely divided condition.

The explosive property, first discovered by accident by Bunsen ⁵ in 1868, appears to be due to the union of occluded oxygen and hydrogen, since the metal is not explosive if prepared in the entire absence of air. Furthermore the explosive metal on being kept at 100° to 200° C. for several days ceases to be explosive.⁶

**Chemical Properties.**—Iridium is not attacked by fluorine in the cold, but on warming to dull redness, vapours of the fluoride are evolved.⁷ Also, when employed as anode in the preparation of fluorine,⁸ it is rapidly attacked. Chlorine at red heat unites with iridium to form the trichloride; a mixture of chlorine and carbon monoxide at 240° C. has no action on the metal ⁹ although platinum is attacked by it.

Finely divided iridium, when heated to redness in air, absorbs a certain amount of oxygen, forming an indefinite mixture of oxides. It is attacked by sulphur vapour at red heat, and under similar conditions phosphorus combines with it to form a fusible phosphate, which decomposes at white heat in a lime furnace, yielding the free metal.

Acids, even aqua regia, have no action on iridium, unless it is very finely divided, in which case it is very slowly attacked.

Fusion with a mixture of potassium hydroxide and nitrate results

---

¹ Paal, Ber., 1917, 50, 722.
⁴ Paal, Ber., 1916, 49, 548.
⁷ Moissan, *Le Fluor et ses Composés*, 1900; Raff, Ber., 1913, 46, 920.
⁸ See this Series, Vol. VIII.
⁹ Antony, *Gazzetta*, 1892, 22, i, 275; 1892, 22, ii, 547.
in the formation of iridates. Fused with potassium hydrogen sulphate it yields the sesquioxides. Alkalis alone have no action when fused with iridium.

Heated for some hours in a Bunsen burning with a smoky flame, an iridium crucible is unharmed, since the deposit of carbon can be entirely burnt away. Sulphur in the gas is likewise without effect. Prolonged ignition with copper renders the metal brittle, but the copper can be burnt off.¹

When strips of iridium are heated to high temperatures in carbon monoxide or in nitrogen, no loss in weight occurs. In carbon dioxide and in nitrogen containing oxygen appreciable losses in weight occur at 1500° C. upwards. This is attributed to the formation of oxide, which is volatile at these high temperatures.²

Atomic Weight.—Approximate Value.—That the atomic weight of iridium is of the order of 193, and not a multiple or submultiple of this amount, may be gathered from several lines of argument. The more important of these may be briefly summarised as follows:

1) The specific heat of iridium between 0° and 100° C. is 0·0828. Application of the Law of Dulong and Petit leads to an atomic weight of 198, the atomic heat being taken as 6·4.

2) A study of the chemical properties of iridium and its compounds shows that, whilst closely resembling platinum in many respects, it forms a fitting link between that element and osmium. With an atomic weight intermediate in value between 190·9 (at. wt. of osmium) and 195·2 (at. wt. of platinum), iridium falls into a suitable position in the Periodic Table where these analogies are recognised.

3) Iridium sulphate unites with the sulphates of the alkali metals to yield a series of well-defined crystalline salts known as alums. These are isomorphous with the better known alums of aluminium, chromium, and iron. Application of Mitscherlich’s Law, therefore, points to their having a composition represented by the general formula:

\[
\text{M}_2\text{SO}_4 \cdot \text{Ir}_3\text{(SO}_4)_3 \cdot 24\text{H}_2\text{O},
\]

that is, a molecule of the salt contains two atoms of iridium. Analyses of these substances prove the atomic weight of iridium, therefore, is 198·1.

Exact Atomic Weight.—The first determination of the atomic weight of iridium is due to Berzelius.³ His single analysis of potassium chloro-

iridate leads to the very high value \( \text{Ir} = 196·7 \).

This value was not supplanted until Seubert’s analyses of ammonium and potassium chloro-

iridate were published in 1878.⁴ The salts were ignited in a stream of hydrogen, and the residual metal weighed; in the case of the potassium salt, of course, the metal was obtained mixed with potassium chloride, which was dissolved out, recovered by evaporation, and weighed. The results were as follow ⁵:

<table>
<thead>
<tr>
<th>Expts.</th>
<th>Formula</th>
<th>Weight</th>
<th>Ir</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>( \text{NH}_4 \text{IrCl}_6 )</td>
<td>100-000</td>
<td>48-782</td>
<td>( \text{Ir} = 193·38 )</td>
</tr>
<tr>
<td>8</td>
<td>( \text{K}_2\text{IrCl}_6 )</td>
<td>100-000</td>
<td>39-880</td>
<td>( \text{Ir} = 192·99 )</td>
</tr>
<tr>
<td>8</td>
<td>( \text{K}_2\text{IrCl}_6 )</td>
<td>2KCl : 100-000</td>
<td>30-820</td>
<td>( \text{Ir} = 192·88 )</td>
</tr>
<tr>
<td>8</td>
<td>( \text{K}_2\text{IrCl}_6 )</td>
<td>4Cl : 100-000</td>
<td>29-291</td>
<td>( \text{Ir} = 193·26 )</td>
</tr>
</tbody>
</table>

² Emsich, Monatsh., 1905, 26, 1011.
⁴ Seubert, Ber., 1878, ii, 1767.
⁵ The antecedent data in the calculations in this section are as follow:

\[
\begin{align*}
\text{O} &= 16·000, \quad \text{N} = 14·008, \quad \text{H} = 1·00762, \quad \text{Cl} = 35·457, \quad \text{K} = 39·100.
\end{align*}
\]
In 1890, Joly determined the percentages of potassium chloride and iridium in the salt \( \text{IrCl}_3 \cdot 3\text{KCl} \cdot 3\text{H}_2\text{O} \), and the percentage of iridium in the salt \( \text{IrCl}_3 \cdot 3\text{NH}_4\text{Cl} \):

3 expts. \( \text{Ir} : 3\text{KCl} : 100-000 : 115:848 \) whence \( \text{Ir} = 193:07 \)
2 expts. \( (\text{NH}_4)_3\text{IrCl}_4 : \text{Ir} : 100-000 : 42:003 \) whence \( \text{Ir} = 193:27 \)

Determinations of the percentage of iridium in ammonium chlor-iridate were made by Hoyermann in 1911:

5 expts. \( (\text{NH}_4)_2\text{IrCl}_4 : \text{Ir} : 100-000 : 43:630 \) whence \( \text{Ir} = 192:59 \)
and by Holzmann in 1912:

4 expts. \( (\text{NH}_4)_2\text{IrCl}_4 : \text{Ir} : 100-000 : 43:784 \) whence \( \text{Ir} = 193:40 \)

The preceding results fall considerably short of the modern standard of atomic weight work, and further determinations of the atomic weight of iridium are desirable. Archibald, in 1909, announced that he had determined the value \( \text{Ir} = 192:90 \) from analyses of potassium iridochloride, but no details of the work have yet been published.

The International Committee's Table for 1918 gives

\[ \text{Ir} = 193:1. \]

**Uses.**—Iridium, both native and alloyed with platinum, is used in the construction of scientific apparatus. The native metal, on account of its hardness, has been employed for pivots, etc. Alloyed with platinum, chiefly for stiffening purposes, it has found application in the manufacture of surgical tools, since it is permanent and non-corrosive. For the same reason the alloy containing 10 per cent. of iridium was used in the construction of the standard metre and kilogram.

Iridium black has been used for producing a black colour in the decoration of porcelain.5

**Alloys.**—With the exception of those obtained with allied metals, the alloys of iridium are unimportant. Osmiridium has already been described, and platinum alloys are dealt with in the sequel (see p. 208). On heating to redness with tin, the compound \( \text{IrSn}_2 \) is obtained in cubical crystals which may be isolated from the excess of tin by treatment with hydrochloric acid, in which the latter dissolves.6

Iridium dissolves in lead, but without forming any definite compound. With copper, a pale red alloy is produced, which is fairly ductile and harder than copper. Nitric acid effects the solution of the lead and copper respectively, in the two foregoing alloys, leaving the iridium behind as an insoluble residue.

Iridium yields no definite compound with zinc, and perhaps not with iron.9

---

1 Joly, *Compt. rend.*, 1890, **110**, 1131.
3 Holzmann, *ibid.*, 1912, 44, 84.
7 Deville and Debray, *Compt. rend.*, 1882, 94, 1557.
Alloys of iridium with silver,\(^1\) gold,\(^2\) ruthenium,\(^3\) osmium,\(^4\) and platinum\(^5\) have been prepared.

Iridium renders platinum stiffer, and is for this reason frequently added to this metal when required for crucibles, etc. For high temperature work it has the disadvantage of rendering the alloy subject to proportionately greater losses in weight at temperatures above 900\(^\circ\) C. in consequence of volatilisation. Below 900\(^\circ\) C., however, and up to a content of 3 per cent. of iridium, the loss in weight on heating is negligible.\(^6\)

*Iridium Amalgam* is not formed by direct union of ordinary iridium and mercury. It has been prepared, however,\(^7\) by triturating with mercury the dull grey, brittle metal saturated with hydrogen after being submitted to prolonged cathodic pulverisation *in vacuo* (see p. 284).

**IRIDIUM AND FLUORINE**

Iridium is not attacked by fluorine in the cold. At dark red heat a reaction sets in, and at a higher temperature a volatile fluoride is obtained in the form of a heavy white vapour.\(^8\)

**IRIDIUM AND CHLORINE**

*Iridium Monochloride*, \(\text{IrCl}\), is obtained \(^9\) by decomposition of the dichloride, \(\text{IrCl}_2\), by ignition in chlorine at about 790\(^\circ\) C., its range of stability being 773\(^\circ\) to 798\(^\circ\) C. in an atmosphere of chlorine. It yields coppery red crystals of density 10.18, which are insoluble in bases and acids, even in concentrated sulphuric acid.

*Iridium Dichloride*, \(\text{IrCl}_2\), was stated to result as an olive-green powder when spongy iridium is heated in a current of chlorine,\(^10\) although Claus\(^11\) regarded the product as a mixture of the free metal and its trichloride. A similar substance is obtained by the action of chlorine on iridium sulphide.\(^12\)

Wöhler and Streicher,\(^13\) however, have prepared the dichloride by ignition of iridium trichloride in chlorine at 770\(^\circ\) C., and thus placed its existence beyond all doubt. It is a crystalline substance, brown in colour, and insoluble alike in acids and bases. Its limits of stability are 768\(^\circ\) to 778\(^\circ\) C. in an atmosphere of chlorine. Above 778\(^\circ\) C. it dissociates into the monochloride and free chlorine.

3. Deville and Debray, *loc. cit.*
4. See p. 212.
5. See p. 280.
For many years, however, it has been known that iridium dichloride can exist in combination with certain other stable salts. Thus, the following complexes have been described: \( \text{IrCl}_2 \cdot \text{H}_2\text{SO}_3 \cdot 4\text{NH}_3\text{Cl} \), \( \text{IrCl}_2 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_4\text{Cl} + 4\text{H}_2\text{O} \), and \( \text{IrCl}_2 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{NH}_3\text{Cl} + 4\text{H}_2\text{O} \).

**Iridium Trichloride**, \( \text{IrCl}_3 \), is most conveniently prepared by heating the reduced metal—obtained by precipitation from an alkali chloriridate solution with magnesium—with sodium chloride in a current of chlorine at 600° to 620° C. The reaction is complete in a few minutes. The limits of stability of the salt under these conditions lie from below 100° C. up to 768° C. Above this latter temperature it dissociates in an atmosphere of chlorine into iridium dichloride and chlorine, and at still higher temperatures (773° C.) into the mono-chloride.

Iridium trichloride is also obtained by heating ammonium chloriridate or iridium tetrachloride in a current of chlorine at 440° C. and cooling the product in an atmosphere of carbon dioxide.

As obtained by the foregoing methods, iridium trichloride is a crystalline substance, olive-green in colour, of density 5-30. It is insoluble in water, alkalis, and acids; even concentrated sulphuric acid and aqua regia having no action upon it. It is appreciably volatile at 470° C.

An almost anhydrous salt is obtained by heating the yellow powder, produced by the action of sulphuric acid upon alkali chloriridites, in hydrogen chloride at temperatures up to 500° C. The colour remains essentially the same, and the composition of the product approaches very closely to that of iridium trichloride, with small quantities of hydrochloric acid and water, the formula being \( \text{IrCl}_3 \cdot m\text{HCl} \cdot n\text{H}_2\text{O} \), where \( m \) and \( n \), however, are but small fractions of unity.

The product is different from ordinary iridium trichloride, however, in that it is deliquescent and soluble in water. On concentrating the solution and drying the product at 100° C. a *sesquihydrate* is obtained, \( 2\text{IrCl}_3 \cdot 3\text{H}_2\text{O} \). This dissolves in water, yielding a greenish yellow solution. Silver nitrate gives, with this solution, a precipitate, which upon drying at 110° C. has the composition \( \text{IrCl}_3 \cdot \text{AgOH} \).

The salt described in earlier literature as the tetrahydrate, \( \text{IrCl}_3 \cdot 4\text{H}_2\text{O} \), appears to be an indefinite mixture of the trichloride with water and hydrogen chloride, as represented by the formula \( \text{IrCl}_3 \cdot m\text{HCl} \cdot n\text{H}_2\text{O} \), where \( m \) is less than unity.

**Hexachloriridites**, \( M_2\text{IrCl}_6 \)

Iridium trichloride readily unites with chlorides of the alkali metals, yielding chloriridites, of general formula \( M_2\text{IrCl}_6 \).

**Potassium Chloriridite**, \( K_2\text{IrCl}_6 \cdot 8\text{H}_2\text{O} \), results (1) when potassium carbonate and chloriridate are heated to redness; (2) on heating potassium chloriridate in hydrogen chloride at 440° C. Some insoluble iridium trichloride is simultaneously produced; (3) it is also formed by reducing a suspension of chloriridate in water with sulphur dioxide, hydrogen sulphide, or nitric oxide. The salt crystallises in olive
prisms,\(^1\) which effloresce in the air, and are readily soluble in water, although insoluble in alcohol.

The \textit{monohydrate}, \(K_3\text{IrCl}_6\cdot\text{H}_2\text{O}\), was prepared by Duffour\(^2\) by the action of hydrochloric acid upon the double oxalates of iridium and potassium at boiling temperature. It yields greenish brown orthorhombic crystals, isomorphous with its rhodium analogue, \(K_3\text{RhCl}_6\cdot\text{H}_2\text{O}\).

The aqueous solution on prolonged boiling deposits an oxychloride in the form of a green powder.\(^3\) Chlorine water or aqua regia converts the salt into the chloriridate. Addition of excess of alkali to a solution of the chloriridate in water does not cause a precipitate to form, since the sesquioxide dissolves as rapidly as formed (\textit{vide infra}), yielding an olive-green solution.

\textbf{Sodium Chloriridite}, \(\text{Na}_3\text{IrCl}_6\cdot12\text{H}_2\text{O}\),\(^4\) is prepared by heating sodium chloriridate to 440° C. in a current of hydrogen chloride.\(^5\) It may also be obtained by reduction of the chloriridate with hydrogen sulphide,\(^6\) or with sodium oxalate.\(^7\)

On concentrating its aqueous solution, blackish green crystals separate out,\(^8\) which melt at 50° C., dissolving in their own water of crystallisation.

\textbf{Ammonium Chloriridite}, \((\text{NH}_4)_3\text{IrCl}_6\cdot\text{Aq.}\), prepared either by reduction of ammonium chloriridate or by decomposing the sodium salt with concentrated ammonium chloride solution,\(^9\) yields dark, olive-green, orthorhombic prisms,\(^10\) which readily dissolve in water.\(^11\) It is probably the \textit{monohydrate}, \((\text{NH}_4)_3\text{IrCl}_6\cdot\text{H}_2\text{O}\).\(^12\) Upon ignition, metallic iridium alone remains, in spongy form. The decomposition begins to be appreciable just above 200° C.

The chloriridites of \textbf{Thallium},\(^13\) \textbf{Silver},\(^14\) \textbf{Rubidium},\(^15\) \textbf{Cæsium},\(^16\) and \textbf{Barium} have been prepared.

\textbf{Aquio Chloriridites}.—The chloriridites are decomposed by treatment with water, yielding aquo derivatives of general formula \(M_2\text{IrCl}_5\cdot\text{H}_2\text{O}\). Thus:

\[
\text{M}_3\text{IrCl}_6 + \text{H}_2\text{O} = \text{M}_2\text{IrCl}_5\cdot\text{H}_2\text{O} + \text{MCl}.
\]

Several of these aquo salts have been isolated.\(^16\)

\textbf{Iridium Tetrachloride}, \(\text{IrCl}_4\), has been prepared in a variety of ways, notably:

(1) By evaporating ammonium chloriridate, \((\text{NH}_4)_3\text{IrCl}_6\), with aqua regia or chlorine water, whereby the ammonia is expelled.

\(^1\) Dufet, \textit{Bull. Soc. Min.}, 1890, 13, 206.
\(^2\) Duffour, \textit{Compt. rend.}, 1915, 255, 222.
\(^3\) Claus, \textit{J. prakt. Chem.}, 1847, 42, 281.
\(^4\) Leidé gives 10\(\text{H}_2\text{O}\). Delépine gives 12\(\text{H}_2\text{O}\).
\(^6\) Claus, \textit{Beiträge zur Chemie der Platinmetalle}, 1854.
\(^7\) Delépine, \textit{Compt. rend.}, 1908, 146, 1287.
\(^8\) Rrhomboedral (Marignac, \textit{Jahresber. Min.}, 1875, p. 138) or monoclinic (Karmrodt and Uhrlaub, \textit{Annalen}, 1852, 81, 120).
\(^9\) Claus, \textit{Beiträge}, etc., p. 75.
\(^12\) Duffour, \textit{loc. cit.}; Joly, \textit{Compt. rend.}, 1890, 110, 1131.
\(^13\) Delépine, \textit{Bull. Soc. chim.}, 1908, [IV], 3, 906; \textit{Compt. rend.}, 1908, 146, 1267; 1909, 49, 1072.
\(^15\) Lang, \textit{ibid.}, 1882, 85, 295.
\(^16\) Delépine, \textit{Compt. rend.}, 1908, 146, 1267.
(2) By dissolving iridium black or the dioxide in hydrochloric acid. The solution is concentrated and any trichloride converted into tetrachloride by addition of aqua regia. The product is dried \textit{in vacuo}, whereby a brownish black amorphous residue is obtained which is very hygroscopic and soluble in water.

(3) Iridium tetrachloride may also be obtained by direct union of the elements,\textsuperscript{1} the chlorine being introduced under high pressure. Thus at 60° C., in the presence of liquid chlorine, under a pressure of about 20 atmospheres, iridium was gradually converted into the tetrachloride in five days; whilst a year was required at 15° C. under a pressure of 8 atmospheres.

Iridium tetrachloride has been obtained crystallised in the form of tetrahedra,\textsuperscript{2} but in this form it contains water, which is expelled, together with hydrogen chloride, on heating. At higher temperatures metallic iridium alone is left as residue.

Iridium tetrachloride is readily reduced to the trichloride. Its aqueous solution, on dilution, yields hypochlorous acid and the trichloride. On boiling, a precipitate of oxychloride is obtained. Addition of excess of alkali precipitates part of the iridium as dioxide, the remainder staying in solution as sesquioxide, being precipitated only upon neutralisation of the alkali. Addition of alcohol to the alkaline solution precipitates metallic iridium, aldehydes and alkali formsates being simultaneously produced. Reducing agents, such as stannous chloride, sulphur dioxide, nitric oxide, hydrogen sulphide, ferrous sulphate, etc., convert the tetrachloride into trichloride.

\textit{Hexachloriridates, }M_2\text{IrCl}_6\textit{ }

Iridium tetrachloride unites with chlorides of the alkali metals to form \textit{chloriridates}, of which the most important are:

\textbf{Potassium Chloriridate, }K_2\text{IrCl}_6\textit{.—This is prepared by heating a mixture of iridium and potassium chloride in chlorine, and purifying the product by crystallisation from its aqueous solution. The mother-liquor contains some chloriridite, which, however, may be converted into the iridate by addition of chlorine water. The salt may also be obtained by decomposing sodium chloriridate with potassium chloride or by boiling a solution of the ammonium salt with potassium hydroxide. It crystallises in black, regular octahedra, which are but slightly soluble in water, and insoluble in saturated potassium chloride solution, as also in alcohol. The aqueous solution on boiling is partially decomposed, yielding the chloriridite. When heated strongly, metallic iridium and potassium chloride remain. Heated to 440° C. in a current of hydrogen chloride, the anhydrous, insoluble trichloride is obtained, together with soluble chloriridite.

Potassium chloriridate is isomorphous with potassium chlorplatinate, K_2\text{PtCl}_6\textit{.}

\textbf{Sodium Chloriridate, }Na_2\text{IrCl}_6\cdot\text{6H}_2\text{O}, \textit{is conveniently prepared in a similar manner to the potassium salt. It also results when solutions of iridium tetrachloride and sodium chloride are mixed and concentrated. The salt crystallises in triclinic prisms\textsuperscript{3} isomorphous with the corresponding platinum salt, Na_2\text{PtCl}_6\cdot\text{6H}_2\text{O}.}

\textsuperscript{1} Wöhler and Streicher, \textit{Ber.}, 1913, 46, 1577.
\textsuperscript{2} Thomson, \textit{Schweigger's J.}, 1826, 47, 59.
\textsuperscript{3} Dufet, \textit{Bull. Soc. Min.}, 1890, 13, 206.
Ammonium Chloriridate, \((\text{NH}_4)_2\text{IrCl}_6\), is readily produced by decomposing the sodium salt with ammonium chloride in aqueous solution.\(^1\) It crystallises in regular octahedra, reddish black in colour, and but slightly soluble in cold water, although appreciably soluble in hot. It does not dissolve in solutions of ammonium or potassium chloride. When evaporated with aqua regia, the ammonia is expelled, iridium tetrachloride remaining. Heated to 440° C. in a current of chlorine the tetrachloride is first formed and decomposes into the anhydrous trichloride.

Ammonium chloriridate is isomorphous with the corresponding chlorplatinate, \((\text{NH}_4)_2\text{PtCl}_6\).

Its solubility in water is given as follows:\(^2\):

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Grams of ((\text{NH}_4)_2\text{IrCl}_6) per 100 grams solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.4</td>
<td>0.694</td>
</tr>
<tr>
<td>26.8</td>
<td>0.899</td>
</tr>
<tr>
<td>39.4</td>
<td>1.124</td>
</tr>
<tr>
<td>52.2</td>
<td>1.583</td>
</tr>
<tr>
<td>61.2</td>
<td>2.068</td>
</tr>
<tr>
<td>69.3</td>
<td>2.746</td>
</tr>
</tbody>
</table>

The solubility of the salt in water between these temperatures is given approximately by the expression:

\[
\text{Solubility} = 0.680 + 0.00044(t - 10).
\]

Rubidium Chloriridate, \(\text{Rb}_2\text{IrCl}_6\), is obtained by mixing a solution of iridium tetrachloride with excess of rubidium chloride, whereby a deep red, crystalline precipitate is obtained. The salt dissolves slightly in hot water to yield an orange-red solution.\(^3\)

Cesium Chloriridate, \(\text{Cs}_2\text{IrCl}_6\), has also been prepared.\(^4\)

Silver Chloriridate, \(\text{Ag}_2\text{IrCl}_6\), is obtained as a fugitive blue precipitate upon adding a solution of the potassium salt to silver nitrate.

When kept, silver chloriridate passes into the yellow chloriridite, \(\text{Ag}_3\text{IrCl}_6\).\(^5\)

Thallium Chloriridate, \(\text{Tl}_2\text{IrCl}_6\), may be prepared in a similar manner to the foregoing salt. It yields small opaque bluish green cubes. When boiled with concentrated hydrochloric acid it is converted into chloriridite, \(\text{Tl}_3\text{IrCl}_6\), which crystallises out in lamellae which are bronze tinted. These are oxidised by nitric acid to the chloriridate again.\(^5\)

Organic Hexachloriridates have also been obtained.\(^6\)

IRIDIUM AND BROMINE

Iridium Tribromide, \(\text{IrBr}_3\cdot 4\text{H}_2\text{O}\), may be obtained by dissolving the hydrated dioxide, \(\text{IrO}_2\cdot 2\text{H}_2\text{O}\), in hydrobromic acid, and evaporating to dryness to decompose the tetrabromide thus formed. Extraction with water and subsequent crystallisation yields olive-green prisms, very soluble in water, but insoluble in alcohol.

At 105–120° C. the water of crystallisation is removed.

---

\(^{1}\) Delépine, \(\text{Compt. rend.}\), 1908, 146, 1267.
\(^{2}\) Rimbach and Korten, \(\text{Zeitsch. anorg. Chem.}\), 1907, 52, 406. Other data were given by Vauquelin, \(\text{Ann. Chim.}\), 1814, 89, 228.
\(^{3}\) Rimbach and Korten, \textit{loc. cit.}
\(^{4}\) Delépine, \(\text{Compt. rend.}\), 1908, 46, 1267.
\(^{5}\) Delépine, \(\text{Compt. rend.}\), 1909, 149, 1072.
\(^{6}\) Rimbach and Korten, \(\text{Zeitsch. anorg. Chem.}\), 1907, 52, 406; Gutbier and his co-workers, \(\text{ibid.}\), 1914, 89, 344.
An Acid Indium Tribromide, $\text{IrBr}_3 \cdot 3\text{HBr} \cdot 3\text{H}_2\text{O}$, is obtained as small, deliquescent, steely blue crystals on working the mother-liquor from the previous salt for a further crop of crystals. It decomposes at 120° C.

Like the trichloride, iridium tribromide unites with bromides of the alkali metals to form bromiridites, the most important of which are:

- **Potassium Bromiridite**, $\text{K}_3\text{IrBr}_6 \cdot 3\text{H}_2\text{O}$, long, olive-green needles;
- **Sodium Bromiridite**, $\text{Na}_3\text{IrBr}_6 \cdot 12\text{H}_2\text{O}$, brownish green rhombohedra;
- **Ammonium Bromiridite**, $\text{(NH}_4\text{)}_3\text{IrBr}_6 \cdot 12\text{H}_2\text{O}$, small olive-green crystals.

**Iridium Tetrabromide** $\text{IrBr}_4$, results when the hydrated dioxide, $\text{IrO}_2 \cdot 2\text{H}_2\text{O}$, is dissolved in hydrobromic acid at a low temperature. On warming it decomposes, yielding the tribromide. With alkali bromides bromiridates are formed.

**Bromiridates**, $\text{M}_2\text{IrBr}_6$

- **Potassium Bromiridate**, $\text{K}_2\text{IrBr}_6$, is readily obtained by double decomposition of sodium chloriridate and potassium bromide.
- It crystallises in bluish black regular octahedra, which are but slightly soluble in water. Aqua regia converts it into potassium chloriridate.
- **Sodium Bromiridate**, $\text{Na}_2\text{IrBr}_6 \cdot \text{aq}$, crystallises in black needles on evaporating a mixed solution of sodium bromide and iridium tetrabromide.
- **Ammonium Bromiridate**, $\text{(NH}_4\text{)}_2\text{IrBr}_6$, separates as small regular octahedra on mixing solutions of sodium bromide and ammonium chloriridate. The crystals are blue in colour, and but slightly soluble in cold water.

**Iridium Oxybromide** has been obtained by heating iridium dioxide to 300° C. in a closed vessel with bromine. It yields black needles, soluble in water, for which the formula $(\text{IrBr}_4)_2\text{IrO}_2$ has been suggested.

**IRIDIUM AND IODINE**

**Iridium Tri-iodide**, $\text{IrI}_3$.—This salt is stated to occur when potassium iodiridate and ammonium chloride solutions are mixed, iodine and the tri-iodide separating out. The former is removed by treating with alcohol, the tri-iodide being left as a greenish powder.

- **Potassium Iodiridite**, $\text{K}_3\text{IrI}_6$, is obtained in the form of small, green crystals by the action of potassium iodide on iridium trichloride.
- **Ammonium and Sodium Iodiridite** have been prepared.

**Iridium Tetra-iodide**, $\text{IrI}_4$, results when a solution of ammonium chloriridate or of iridium chloride in hydrochloric acid is boiled with potassium iodide. It is precipitated as a black, insoluble powder, which decomposes at 100° C.

**Potassium Iodiridate**, $\text{K}_2\text{IrI}_6$, is formed when a solution of iridium chloride is added to one of potassium iodide. The solution is filtered, and the iodiridate obtained on crystallisation as dark brown octahedra.

**Sodium** and **Ammonium Iodiridates** have been prepared.

---

IRIDIUM AND OXYGEN

Iridium Monoxide, IrO.—It is doubtful if this oxide has ever been obtained in the free state.\(^1\)

Iridium Sesquioxide, \(\text{Ir}_2\text{O}_3\), is obtained by igniting iridium sulphite, or by heating an alkali chloriridite with twice its weight of carbonate. The product is washed with hot water, and the colloidal residue treated with a solution of ammonium chloride to effect its coagulation, and finally with nitric acid and dried, the acid serving to remove the last traces of alkali.\(^2\)

In an impure form iridium sesquioxide is obtained by mixing hot solutions of potassium hydroxide and sodium chloriridite in an atmosphere of carbon dioxide. The solution is evaporated to dryness, and the residue heated to redness in a current of carbon dioxide. Further purification is effected by boiling first with sodium hydroxide solution and then with sulphuric acid.\(^3\)

When heated above 400° C. iridium sesquioxide decomposes, yielding metallic iridium and its dioxide, a little oxygen being likewise liberated. It dissolves in hydrochloric acid, yielding a colloidal solution.

Hydrated Iridium Sesquioxide, \(\text{Ir}_2\text{O}_3.5\text{H}_2\text{O}\), is obtained as an olive-green precipitate on addition of the requisite quantity of potassium hydroxide solution to one of chloriridite. If excess of potash is taken no precipitate appears, since the sesquioxide dissolves as rapidly as formed, yielding an olive-green solution, from which, however, it is precipitated on addition of acid.

The precipitated oxide readily oxidises in air. It dissolves in acids to a yellowish green solution. The alkaline solutions readily oxidise on boiling in air or on addition of hydrogen peroxide, the dioxide being precipitated (vide infra). Boiling them with alcohol causes reduction to iridium black.\(^4\)

Iridium Dioxide, \(\text{IrO}_2\), is obtained when potassium iridate, \(\text{IrO}_3.2\text{K}_2\text{O.3H}_2\text{O}\), is heated with excess of potassium bromide and chloride. The melt is extracted with water, the insoluble residue treated with aqua regia to dissolve any unchanged iridate, and finally dried at 100° C. The product thus obtained is pure, crystalline iridium dioxide.\(^5\)

The same oxide results, but in an amorphous condition, when finely divided iridium is heated in a current of air or oxygen to bright redness. For complete oxidation the reaction must be continued for many hours, until a constant weight has been reached,\(^6\) the metal becoming black. The optimum temperature for this reaction is 1070° C.\(^7\)

Finally the anhydrous dioxide is obtained by heating the hydrated oxide to 760° C.

When heated, iridium dioxide decomposes into oxygen and the

---

2 Claus, loc. cit.
4 Birnbaum, Annalen, 1865, 136, 177.
5 Geisenheimer, Compt. rend., 1890, 110, 855.
6 Geisenheimer, loc. cit.
7 Wöhler and Witzmann, Zeitsch. Elektrochem., 1908, 14, 97.
metal. The dioxide and metal are mutually soluble to a certain extent, so that after a certain amount of decomposition has occurred the solid phase consists of two saturated solutions, and yields a constant dissociation pressure.1

Iridium dioxide is readily reduced to the metal by heating in hydrogen.

**Hydrated Iridium Dioxide**, IrO$_2$.2H$_2$O, results (1) when excess of caustic alkali is added to a solution of chloriridate of or iridium tetra-chloride. Any sesquioxide simultaneously produced passes into solution, but is converted into the dioxide by boiling in air, by addition of hydrogen peroxide, or by passing a current of oxygen through the solution.

(2) On addition of alkali in the presence of air to a double sulphate of iridium.2

(3) On boiling for several hours crystals of potassium iridate in a solution of ammonium chloride. The crystals are gradually converted into a flocculent precipitate of hydrated dioxide, ammonia being simultaneously evolved.5 A similar precipitate is obtained on boiling the blue solution formed during the preparation of potassium iridate (vide infra) with excess of ammonium chloride.

The precipitated oxide can be obtained in a very pure state in this manner, by drying in carbon dioxide at 400° C., then boiling with alkali once more, and finally with sulphuric acid.4

(4) On heating to redness for two or three hours a mixture of finely divided iridium and sodium hydroxide and nitrate. The mass is extracted with water, leaving the hydrated oxide as residue.5 Probably a sodium iridate, analogous to the potassium salt, is formed, which, being unstable, is decomposed during the extraction with water.

The colour of iridium dioxide depends to a large extent upon the hydration. Dried over concentrated sulphuric acid it contains two molecules of water and is black in colour. When heated to 760° C. it becomes anhydrous.

**Colloidal Iridium Dioxide** is obtained by mixing solutions of potassium hydroxide and chloriridate in the cold, the solution gradually becoming violet in colour,4 and finally the violet dioxide separates out.

When boiled, the violet solution becomes blue, attributable, perhaps, to aggregation of colloidal particles.

Iridium dioxide also exists in colloidal form in solutions obtained by dissolving the amorphous oxide in hydrochloric acid.

The monohydrate, IrO$_2$.H$_2$O, does not appear to exist, but the potassium salts, 6IrO$_2$.K$_2$O and 12IrO$_2$.K$_2$O, are claimed to have been isolated.5

**Iridium Trioxide**, IrO$_3$, has not been isolated in a pure state, and appears to be unstable in the absence of alkali. Oxygen is absorbed when the dioxide is heated with alkali in oxygen, but not in the amount theoretically required to convert the whole into trioxide.4

The potassium salt, K$_2$O.2IrO$_3$, is described as resulting when potassium nitrate and iridium are fused together.6

---

1 Wöhler and Witzmann, Zeitsch. Elektrochem., 1908, 14, 97.
2 Lecoq de Boisbaudran, Compt. rend., 1883, 96, 1336, 1406, 1551.
3 Geisenheimer, loc. cit.
4 Wöhler and Witzmann, Zeitsch. anorg. Chem., 1908, 57, 323.
5 See Leidié and Joly, Compt. rend., 1895, 120, 1341.
Another potassium salt, \( \text{IrO}_2 \cdot 2\text{K}_2\text{O} \cdot \text{H}_2\text{O} \), is said to be obtained on heating for a couple of hours finely divided iridium with a mixture of potassium hydroxide and nitrate. The black crystalline mass resulting is readily soluble in potash solution, to which it imparts a blue colour.\(^1\)

**IRIDIUM AND SULPHUR**

**Iridium Monosulphide**, \( \text{IrS} \), is stated to result on heating finely divided iridium to redness in sulphur vapour,\(^2\) but it is doubtful if it has ever been obtained as a separate chemical entity.

**Iridium Sesquisulphide**, \( \text{Ir}_2\text{S}_3 \), is formed by passing hydrogen sulphide into a slightly acid solution of a chloriridate at \( 100^\circ \text{C} \).

It is a black, colloidal substance, soluble in aqua regia, giving an iridium chloride, and decomposable at high temperatures, yielding metallic iridium.

**Iridium Disulphide**, \( \text{IrS}_2 \), has been prepared in a variety of ways, chief among which are:

1. Heating ammonium chloriridate with sulphur.\(^3\)
2. Acting on finely divided iridium with an alkali polysulphide.\(^4\)
3. Passing hydrogen sulphide over lithium chloriridate at 4–7\(^\circ\) \text{C}.

No action takes place below 0\(^\circ\) \text{C}., whilst above 10\(^\circ\) \text{C} the salt is rapidly attacked, free sulphur separating. The product is repeatedly extracted with absolute alcohol and dried at 90–100\(^\circ\) \text{C} in carbon dioxide.\(^5\)

Iridium disulphide is a brown powder. Moist air has no action on it. Heated to 300\(^\circ\) \text{C} in air, sulphur is expelled, metallic iridium remaining behind. Hydrochloric and nitric acids do not affect it although fuming nitric acid and aqua regia effect its decomposition. It is reduced to a lower sulphide at red heat in a current of carbon dioxide.

**Iridium Sesquisulphite**, \( \text{Ir}_5(\text{SO}_3)_2 \), may be obtained by exposing a suspension of the hydrated dioxide in water to a current of sulphur dioxide. The liquid becomes greenish in colour, and on standing deposits a yellow, crystalline precipitate of iridium sulphite.\(^6\) This salt is but slightly soluble in water. Alkalies convert it into the sesquisulphate, which, upon exposure to air, oxidises to the dioxide. Acids liberate sulphur dioxide, converting the residue into the corresponding salt of iridium. When ignited, sulphur dioxide is expelled and a residue of iridium sesquisulphide is obtained.

A second substance containing sulphur dioxide is described by Birnbaum as formed as a black, amorphous, insoluble residue during the preparation of the foregoing sesquisulphite. He regards it as a basic sulphite of tetravalent iridium, \( \text{IrO}_2 \cdot \text{SO}_2 \cdot 4\text{H}_2\text{O} \), but it may equally well be a basic sulphate.

Iridium sesquisulphite combines with sulphites of the alkali metals to yield double salts. Of these the best known are:

**Potassium Iridium Sulphite**, \( 3\text{K}_2\text{SO}_3 \cdot \text{Ir}_2(\text{SO}_3)_3 \cdot 6\text{H}_2\text{O} \), which may be written as \( \text{K}_2\text{Ir}(\text{SO}_3)_3 \cdot 3\text{H}_2\text{O} \), to show an analogy with the constitutions

---

\(^1\) See Geisenheimer, *Compt. rend.*., 1890, 110, 855.
\(^5\) Antony, *Gazzetta*, 1893, 23, 1, 190.
of the iridi-nitrites and iridi-cyanides described in the sequel. The salt is obtained as a brown, crystalline, insoluble mass on adding potassium carbonate to a solution of iridium sulphite.\(^1\)

Closely resembling the foregoing salt is the ammonium derivative, \(3(\text{NH}_4\text{)SO}_4\cdot\text{Ir}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}\). The complex chlor-sulphites:

\[
2\text{K}_2\text{SO}_3\cdot\text{IrCl}\cdot\text{SO}_3,\quad 3\text{KCl}\cdot\text{K}_2\text{SO}_3\cdot\text{IrCl}_2\cdot\text{SO}_3\cdot2\text{H}_2\text{O},
\]

\[
2\text{K}_2\text{SO}_3\cdot\text{KSO}_3\cdot\text{IrCl}_2\cdot2\text{KCl}\cdot12\text{H}_2\text{O},\quad \text{and IrCl}_2\cdot4\text{NH}_4\text{Cl}\cdot\text{H}_2\text{O}
\]

have also been prepared.\(^2\)

**Sodium** yields a sulphite, of formula \(3\text{Na}_2\text{SO}_3\cdot\text{Ir}_2(\text{SO}_4)_3\cdot8\text{H}_2\text{O}\), obtained in a similar manner to the ammonium and potassium salts.\(^1\)

An acid sulphite, \(3\text{Na}_2\text{SO}_3\cdot\text{H}_2\text{SO}_3\cdot\text{IrSO}_3\cdot\text{Aq.}\), and a neutral sulphite of formula \(3\text{Na}_2\text{SO}_3\cdot\text{IrSO}_3\cdot10\text{H}_2\text{O}\), have been described.\(^3\) It is difficult to believe, however, that many of the foregoing complexes are definite chemical entities.

**Iridium Sesquisulphate**, \(\text{Ir}_2(\text{SO}_4)_3\cdot2\text{H}_2\text{O}\), is obtained by dissolving the hydrated sesquioxide in dilute sulphuric acid and allowing it to crystallise in the absence of air.\(^4\)

Unless special precautions are taken, the product has a violet colour due to the presence of iridium in a higher state of oxidation. By effecting the preparation of the salt in *vacuo* yellow crystals of sesquisulphate are obtained, which dissolve in water to a bright yellow solution. Exposure to air causes the solution to turn violet immediately, particularly if the solution is dilute.

**Iridium Alums**, \(\text{M}_2\text{SO}_4\cdot\text{Ir}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}\)

Iridium sulphate, like the sulphates of cobalt and rhodium, unites with the sulphates of the alkali metals to yield a series of well-defined crystalline salts known as alums. These are isomorphous with the better known alums of aluminium, chromium, manganese, and iron, and form an interesting link between these metals and the central vertical column in Group VIII, of which iridium is the lowest member.

**Potassium Iridium Alum**, \(\text{K}_2\text{SO}_4\cdot\text{Ir}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}\), is obtained\(^5\) by mixing the requisite quantities of solutions of potassium sulphate and iridium sesquisulphate in *vacuo* and concentrating over sulphuric acid. After several days the salt crystallises out from the syrupy solution as yellow octahedra. These begin to melt at about 96° C., and completely melt at 102° to 103° C. In a hot-air bath they lose all their combined water, becoming green and then violet in colour. The product, however, remains soluble in water, unless the temperature of desiccation exceeds 400° C. At red heat a basic sulphate is obtained as well as metallic iridium.

**Ammonium Iridium Alum**, \((\text{NH}_4)_2\text{SO}_4\cdot\text{Ir}_2(\text{SO}_4)_3\cdot24\text{H}_2\text{O}\), prepared in a similar manner to the preceding salt,\(^5\) crystallises in yellowish red octahedra, which melt at 105° to 106° C., yielding a reddish violet liquid. On heating still further the combined water is gradually expelled, whilst at red heat metallic iridium is obtained as residue.

---

Cesium Iridium Alum, Cs₂SO₄·Ir₂(SO₄)₃·24H₂O, yields bright yellow, octahedral crystals, melting at 109° to 110°C, to a yellowish red liquid. Its aqueous solution is yellow, becoming rose-coloured on warming above 40°C. The crystals become anhydrous at 300° to 350°C.

Rubidium Iridium Alum, Rb₂SO₄·Ir₂(SO₄)₃·24H₂O, crystallises in pale yellow octahedra. Both in the solid state and in solution this alum is stable in air. It melts at 108° to 109°C, yielding a yellowish red liquid.

Thallium Iridium Alum, Tl₂SO₄·Ir₂(SO₄)₃·24H₂O, crystallises in golden-yellow octahedra.

Iridium Disulphate, Ir(SO₄)₂, is obtained as a yellowish brown, amorphous mass on oxidising iridium sulphide with concentrated nitric acid. On gently warming, the reaction takes place with vigour, and, when complete, the nitrous fumes are expelled by repeated evaporation and re-solution in water. It does not appear to yield double salts, and on warming with concentrated sulphuric acid yields iridium sesquisulphate.

Complex Iridium Disulphates.—Two series of salts known as disulphates have been prepared, namely:

1. Green salts of the type M₂[Ir(SO₄)₂·OH]·H₂O, and
2. Reddish brown salts of the type M₃[Ir(SO₄)₂·(OH)₂],
where M stands for a monovalent metal.

Of these the former salts are usually acidic, whilst the latter are basic. They are readily converted, the one into the other, by addition of acid or base, as occasion requires. Several such salts have been prepared.

IRIDIUM AND SELENIUM

Iridium Sesquiselenide, Ir₂Se₃, is obtained as a black precipitate by the action of hydrogen selenide upon a hot solution of iridium trichloride. It is amorphous, insoluble in nitric acid even on warming, but slowly attacked by fuming nitric acid in sealed tubes at 250°C and by aqua regia.

A compound of selenium and iridium, but of indefinite composition, is obtained by heating the two elements together at red heat in sealed tubes. The product is black, and very resistant to acid attack.

IRIDIUM AND NITROGEN

Hydrogen Iridi-nitrite, H₃Ir(NO₂)₆, is stated by Gibbs to crystallise in yellow prisms which are readily soluble in water. The hydrogen may be replaced by metals yielding a series of salts known as iridi-
nitrites, of general formula $M_3\text{Ir(NO}_2\text{)}_6$, and analogous to the cobalti-nitrites and rhodi-nitrites already considered.

Iridi-nitrites, $M_3\text{Ir(NO}_2\text{)}_6$

Of these the most important salt is:

Potassium Iridi-nitrite, $K_3\text{Ir(NO}_2\text{)}_6$, which is conveniently prepared by adding sodium nitrite to a hot acidulated solution of sodium chlor-iridite until it is bleached. The solution is boiled to expel nitrous oxides, and potassium chloride is added in excess, whereupon iridium potassium nitrite is precipitated as a white mass.

It is also formed by adding potassium nitrite to a solution of iridium sulphate in the warm. It is a white powder, which readily dissolves in boiling water, but which is insoluble in potassium chloride solution.

At $300^\circ$ C. it begins to decompose, whilst at $440^\circ$ C. decomposition is rapid. Heated in vacuo at this latter temperature, nitrogen and nitric oxide are liberated, a greenish black powder remaining behind.

This, on treatment with water, leaves after a time a heavy black powder consisting of $6\text{IrO}_5\cdot K_3\text{O}$, which it is suggested is probably the salt of the hypothetical hexiridous acid, $(\text{IrO})_6\text{O}_5(\text{OH})_2$ or $6\text{IrO}(\text{OH})_2 - 5\text{H}_2\text{O}$. When the double nitrite is heated to redness in a muffle, the residue on thorough washing has the composition $12\text{IrO}_2\cdot K_3\text{O}$, which Joly and Leidi suggest may be the potassium salt of the hypothetical dodeca-iridous acid, $(\text{IrO})_2\text{O}_{11}(\text{OH})_2$ or $12\text{IrO}(\text{OH})_2 - 11\text{H}_2\text{O}$. It is very doubtful, however, if we are justified in assuming that these are separate chemical entities.

Sodium Iridi-nitrite, $\text{Na}_3\text{Ir(NO}_2\text{)}_6\cdot \text{H}_2\text{O}$, is readily prepared by adding sodium nitrite to a solution of iridium sulphate in the warm. It is readily soluble in water.

Ammonium Iridi-nitrite, $(\text{NH}_4)_3\text{Ir(NO}_2\text{)}_6$, may be prepared by addition of sodium nitrite and ammonium sulphate to a warm solution of iridium sulphate. It separates out as a white powder, similar to the potassium salt. When boiled with water it evolves nitrogen, and heated in the dry state it detonates.

Iridium Chlor-nitrites

Potassium Iridium Chlor-nitrites.—Several of these have been described.

The dinitro-tetrachlor-iridite salt, $K_3\text{IrCl}_4\cdot (\text{NO}_2)_3$, results on treating ammonium chloriridate suspended in water with nitrogen trioxide, and then adding the requisite quantity of potassium chloride. It crystallises out as golden yellow crystals, very soluble in water. When boiled with potassium nitrite it yields the trinitro-trichlor derivative, $K_3\text{IrCl}_6(\text{NO}_2)_3$.

Sodium Iridium Chlor-nitrite, $\text{Na}_3\text{IrCl}_6\cdot 3\text{Na}_3\text{Ir(NO}_2\text{)}_6$.—This salt was obtained by Lang by mixing solutions of sodium nitrite and chlor-

1 Leidié, Compt. rend., 1902, 134, 1582.
2 Joly and Leidié, Compt. rend., 1895, 120, 1341.
3 Gibbs, Ber., 1871, 4, 280; Leidié, Compt. rend., 1902, 134, 1582.
4 Leidié, Compt. rend., 1902, 134, 1582; Bull. Soc. chim., 1902, 27, [iii], 936.
5 Miolati and Gialdini, Atti R. Accad. Lincei, 1902, 17, [ii], 151; Leidié, Compt. rend., 1902, 134, 1582; Quennessen, Compt. rend., 1905, 141, 258.
6 Leidié (Compt. rend., 1902, 134, 1582) simultaneously prepared this salt by the direct action of potassium nitrite on potassium chloriridate.
iridate. It is formed as a white precipitate but very slightly soluble in cold water.

**Iridium Chlor-nitrites of Barium**,\(^1,2\) \(\text{Ba}_3(\text{IrCl}_6)_2 \cdot 3\text{Ba}_2\text{Ir}_2(\text{NO}_2)_4\); **Cæsium**,\(^3\) \(\text{Cs}_2(\text{NO}_2)_2 \cdot 2\text{IrCl}_4\); **Lead**,\(^3\) \(\text{Pb}_3(\text{NO}_2)_4 \cdot 2\text{IrCl}_4 \cdot 2\text{Pb(OH)}_2\); **Mercury**,\(^3\) \(\text{Hg}_3(\text{NO}_2)_4 \cdot 2\text{IrCl}_4\); and **Silver**,\(^3\) \(\text{Ag}_3(\text{NO}_2)_4 \cdot 2\text{IrCl}_4\) have all been described.

**IRIDIUM AND PHOSPHORUS**

**Iridium Phosphide**, \(\text{IrP}_3\), results on heating iridium with phosphorus,\(^4\) as a brilliant and hard mass, insoluble in acids.

Numerous phospho-chlorides, phospho-bromides, and other complex derivatives of iridium have been prepared by Geisenheimer.\(^5\)

**IRIDIUM AND CARBON**

Iridium and carbon do not appear to unite to form a definite carbide, although when the two elements are heated together in the electric furnace iridium absorbs a certain amount of carbon which, on solidification, is given up again as graphite.\(^6\)

**Iridium Cyanide**, \(\text{Ir} \cdot (\text{CN})_6\), is believed to result when acids are allowed to act upon hydrogen iridicyanide.\(^7\)

**Hydrogen Iridicyanide**, \(\text{H}_3\text{Ir} \cdot (\text{CN})_6\), is conveniently prepared \(^7\) by treating its barium salt with the requisite quantity of dilute sulphuric acid. On shaking with ether a white crystalline deposit of hydrogen iridicyanide is obtained.

The crystals resemble those of their cobalt analogue, \(\text{H}_3\text{Co} \cdot (\text{CN})_6\), in that they are very soluble in water and exhibit a strongly acid reaction, readily decomposing carbonates. They combine with bases to form well-defined salts. Conductivity measurements of the potassium and barium salts show that they are not simply double cyanides, but salts of hydrogen iridicyanide.\(^8\)

**Potassium Iridicyanide**, \(\text{K}_3\text{Ir} \cdot (\text{CN})_6\).

Pure iridium, when heated in a finely divided condition to a dull glow with potassium cyanide, yields a double cyanide.

The yield, however, is poor. A better method is to heat ammonium chloriridate with a slight excess of potassium cyanide for ten to fifteen minutes.\(^9\) Extraction of the melt with boiling water and subsequent evaporation yields crystals of the potassium iridicyanide, the other constituents, namely, potassium chloride and cyanide, being more soluble and remaining in solution.

Potassium iridicyanide yields \(^8\) hexagonal crystals \((a : c = 1 : 1 \cdot 3319)\) which are colourless, transparent, and stable in air. The crystals

---

5. Geisenheimer, Compt. rend., 1890, 110, 1004, 1336; 1890, 111, 40.
9. Claus, Beiträge zur Chemie der Platinmetalle, 1884, p. 96.
dissolve in water easily, but only with difficulty in alcohol. The solution yields precipitates of various colours with salts of the heavy metals. With ferrous salts a white precipitate is obtained; with ferric, a bright yellow. Acetic acid is without action on potassium iridicyanide, although it decomposes the corresponding rhodicyanide. This affords, therefore, a useful method of separating rhodium from iridium.

**Barium Iridicyanide**, $\text{Ba}_3(\text{IrC}_6\text{N}_6)_4\cdot18\text{H}_2\text{O}$, was obtained by Martius \(^1\) as the result of treating the copper salt with excess of barium hydroxide solution. The excess of barium is removed by passage of carbon dioxide through the liquid, and upon slow evaporation the salt separates out in large trimetric crystals. Exposed to dry air the crystals effloresce, still, however, containing six molecules of water, which are completely expelled at 100° C.

**Silver Iridicyanide**, $\text{Ag}_3\text{Ir}($CN$)_6$, has also been obtained \(^2\) as a white, flocculent precipitate on adding silver nitrate to a solution of the potassium salt.

**Detection and Estimation of Iridium.**—See Chapter X.

---

CHAPTER IX
PLATINUM AND ITS COMPOUNDS

PLATINUM

Symbol, Pt. Atomic weight, 195.2 (O = 16)

Occurrence and History.—Platinum occurs in nature, sometimes in a fairly pure state, but more usually alloyed with allied elements, in the so-called platinum ores. It is generally found as grains or scales, but occasionally as irregular lumps or nuggets ranging in weight from anything up to 20 lb. Native crystals are rare, cubes being the most frequent form. The hardness of native platinum ranges from 4 to 4.5, and density from 14 to 19.

Two varieties of native platinum are known, namely:
1. Non-magnetic.—This is the more usual form, and has the greater density, namely, 16.5 to 18.
2. Magnetic.—Density circa 14. The magnetic property appears to bear some relation to the percentage of iron contained in the alloy, but strict proportionality in no way exists. Some specimens of native platinum from the Urals, indeed, are said to attract iron filings even more powerfully than an ordinary magnet.

Platinum was probably first discovered in the alluvial deposits of the River Pinto in the province of Choco, Columbia (S. America). It was first brought to Europe in 1735, and received its name from the Spanish plata, silver, in consequence of its white appearance.

Native platinum has also been found in Brazil along with gold in syenite; in alluvial material amongst the Urals; in sand from the Ivalo River, N. Lapland, associated with the diamond; as well as in Borneo; in the sands of the Rhine; in County Wicklow, Ireland; in New Zealand, New South Wales, California, British Columbia and the Yukon River, and in Spain.

The mining of platinum in British Columbia dates from 1885. Much of the ore is coarse and has the rough, unworn appearance of nuggets that have not travelled far from their original source. The nuggets are rarely large, and seldom exceed half an ounce (14 grams) in weight. Most of the metal occurs in small grains which can be separated into magnetic and non-magnetic, the latter forming the greater proportion of the total.

1 See Sosman and Hostetter, J. Washington Acad. Sci., 1915, 5, 293; Daubree, Compt. rend., 1875, 80, 626.
3 Analyses of platiniferous chromite from the Urals are given by Cerdan and de Rubies, Anal. Fis. Quim., 1915, 13, 155.
5 For a summary of the records of the occurrence of platinum in Spain see de Rubies, Anal. Fis. Quim., 1915, 13, 420; also de Oraeta and de Rubies, Compt. rend., 1916, 162, 45.
The largest nugget of platinum ever yet found weighed 21 lb. troy, or 7837 grams, and was deposited in the Demidoff Museum at Petrograd.

Native platinum frequently contains traces of nickel, as evidenced by the spectrochemical examination of specimens from Russia, Spain, and America. A sample from Kitlim, for example, contained 0.1 per cent. of nickel or more. Only one previous analysis of platinum appears to have been recorded, containing nickel, namely, a magnetic platinum from Nizhne-Tagilsk, in which 0.75 per cent. of nickel was present. Platinum ores rich in iron yield the most intense nickel spectrum.

In the following table are given the mean analyses of native platinum obtained from various mines in the Urals:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>77.55</td>
<td>85.10</td>
<td>77.61</td>
<td>88.50</td>
<td>60.58</td>
<td>82.46</td>
</tr>
<tr>
<td>Osmium</td>
<td>1.44</td>
<td>4.17</td>
<td>10.88</td>
<td>0.79</td>
<td>20.13</td>
<td>4.98</td>
</tr>
<tr>
<td>Iridium</td>
<td>2.56</td>
<td>1.88</td>
<td>6.39</td>
<td>2.74</td>
<td>6.72</td>
<td>1.79</td>
</tr>
<tr>
<td>Rhodium</td>
<td>0.52</td>
<td>0.80</td>
<td>0.48</td>
<td>0.62</td>
<td>0.74</td>
<td>0.69</td>
</tr>
<tr>
<td>Palladium</td>
<td>0.26</td>
<td>0.80</td>
<td>0.32</td>
<td>0.28</td>
<td>0.19</td>
<td>0.18</td>
</tr>
<tr>
<td>Copper</td>
<td>3.27</td>
<td>0.63</td>
<td>1.95</td>
<td>1.14</td>
<td>0.52</td>
<td>0.54</td>
</tr>
<tr>
<td>Iron</td>
<td>14.46</td>
<td>7.86</td>
<td>2.60</td>
<td>11.05</td>
<td>11.08</td>
<td>9.49</td>
</tr>
</tbody>
</table>

The table on page 258 gives analyses of native platinum found in various other parts of the world, and from it the reader will obtain a fair idea of the variations in composition usually encountered.

Platinum is found in combination with arsenic as the rare mineral sperrylite, PtAs₂, at Vermillion Mine in Ontario, Canada. It was first discovered by Sperry (whence its name) in 1887 along with copper and iron pyrites in contact with gold ore. It crystallises in cubes or, less frequently, in octahedra; hardness, 6–7; specific gravity, 10.602 at 20°C. It is tin-white in colour, possessed of metallic lustre, and contains traces of rhodium and antimony.

Sperrylite occurs in small quantities in the nickel ores of Sudbury, Ontario (see p. 82), the actual percentage of platinum being directly proportional to the copper content of the ore, that is, proportional to the amount of copper pyrites. It occurs in small crystalline fragments disseminated throughout the mass of the ore.

Platinum has also been detected in meteoric iron.

---

Preparation.—Several methods have been tried for the separation of platinum from its alloys. By a series of washing processes the sand and gravel are removed from the ore, and if any gold is present it finds

3. H. L. Wells, Amer. J. Sci., 1889 [iRI], 37, 67; Penfield, ibid., p. 71. See also Walker, Zeitsh. Kryst. Min., 1896, 25, 561; Amer. J. Sci., 1896, [iv], 1, 110; Wells and Penfield, ibid., 1902, [iv], 13, 95; Dickson, ibid., 1903, [iv], 15, 137.
5. Dickson, ibid., 1903, [iv], 15, 137.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>78.25</td>
<td>82.98</td>
<td>86.88</td>
<td>17.30</td>
<td>0.80</td>
<td>0.86</td>
<td>0.91</td>
<td>0.98</td>
<td>0.92</td>
<td>0.93</td>
</tr>
<tr>
<td>Trinidad</td>
<td>70.90</td>
<td>70.60</td>
<td>70.80</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>0.92</td>
<td>0.91</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>Columbus</td>
<td>72.96</td>
<td>72.78</td>
<td>72.98</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>0.92</td>
<td>0.91</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>Colombia</td>
<td>78.82</td>
<td>78.82</td>
<td>78.82</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>0.92</td>
<td>0.91</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>California</td>
<td>76.60</td>
<td>76.60</td>
<td>76.60</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>0.92</td>
<td>0.91</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>Oregon</td>
<td>51.45</td>
<td>41.70</td>
<td>41.70</td>
<td>6.80</td>
<td>6.80</td>
<td>0.85</td>
<td>2.95</td>
<td>2.95</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Spain</td>
<td>59.80</td>
<td>59.80</td>
<td>59.80</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>1.00</td>
<td>1.00</td>
<td>1.10</td>
<td>1.10</td>
</tr>
<tr>
<td>Australia</td>
<td>61.40</td>
<td>61.40</td>
<td>61.40</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>1.20</td>
<td>1.20</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>Borneo</td>
<td>69.90</td>
<td>70.60</td>
<td>70.60</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>1.40</td>
<td>1.40</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>British Columbia</td>
<td>72.97</td>
<td>72.97</td>
<td>72.97</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>1.60</td>
<td>1.60</td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>Plattesburg</td>
<td>82.91</td>
<td>82.91</td>
<td>82.91</td>
<td>11.04</td>
<td>18.93</td>
<td>0.93</td>
<td>1.80</td>
<td>1.80</td>
<td>1.90</td>
<td>1.90</td>
</tr>
</tbody>
</table>
its way into the concentrate along with the crude platinum, to be subsequently removed. In Russia the gold is abstracted by repeated amalgamation with mercury, and the crude platinum, without further treatment, is mostly exported.

Refining Crude Platinum.—The crude platinum is digested with aqua regia (one part HNO₃ at 85° to 86° Beaumé, and three parts HCl at 20° B.) whereby the platinum and several allied elements are completely dissolved, leaving a residue of osmiridium and sand, together with a little graphite. The solution is diluted, filtered, and evaporated to a syrup. Hydrochloric acid is added to decompose nitroso compounds, the whole taken to dryness and heated to 150° C. to expel the nitric acid and to simultaneously convert the palladium to palladous chloride. The platinum is now precipitated as ammonium chlor-platinate by addition of ammonium chloride. This is separated, washed, and finally heated to redness in a muffle, whereby spongy platinum is obtained, the ammonium chloride and chlorine being expelled.

\[(\text{NH}_4)_2\text{PtCl}_6 = \text{Pt} + 2\text{NH}_4\text{Cl} + \text{Cl}_2.\]

The spongy metal is now made into a paste with water, compressed into a mould, and either forged into a homogeneous bar by heating and hammering, or melted in an oxyhydrogen furnace constructed of lime.

As obtained in this way the platinum usually contains some 2 per cent. of iridium, precipitated along with the ammonium chlor-platinate as the corresponding iridium salt. A second refining serves to remove this iridium, a fairly pure platinum resulting.

The solution from which the ammonium chlor-platinate has been separated still contains a little platinum with practically all the rhodium, ruthenium, and palladium. All are precipitated by metallic iron and dissolved in aqua regia. Addition of more ammonium chloride effects the precipitation of the remaining platinum, and the filtrate may be worked for the other metals (see p. 154).

At Hanau the method adopted is similar to the foregoing. The crude Russian platinum is treated with a mixture of aqua regia (one part) and water (two parts) in a glass retort under a pressure of 12 inches of water. The resulting solution is evaporated to dryness and heated to 125° C., whereby the palladium is converted to the palladous condition. The product is extracted with water, and acidified with hydrochloric acid. On addition of ammonium chloride a precipitate of ammonium chlor-platinate is obtained, contaminated with some ammonium chlor-iridate. On concentration of the mother-liquor a further small amount of ammonium chlor-iridate separates out. The liquid is now treated with scrap-iron, which precipitates all the other platinum metals, together with any platinum and iridium not hitherto precipitated. The deposit is washed free from undissolved iron by treatment with hydrochloric acid, and in turn dissolved in aqua regia. From this

1 For further details see Gowland, The Metallurgy of the Non-ferrous Metals (Chas. Griffin and Co., 1918).
3 Deville and Debray (Ann. Chim. Phys., 1861, [iii], 6r, 74) and Heraeus (Zeitsch. anal. Chem., 1892, 3r, 310) have recommended operating in a closed flask under a slightly greater pressure than atmospheric.
solution platinum and iridium are thrown out as ammonium chlor-platinate and chlor-iridate respectively, by addition of ammonium chloride. The mother-liquor contains ruthenium, rhodium, palladium, osmium, and some iridium. The ammonium chlor-platinate, mixed with small quantities of chlor-iridate, is ignited, and the spongy metal thus obtained treated in the manner described above.

Another method consists in fusing finely powdered crude platinum with two or three times its weight of zinc. The brittle alloy thus formed is powdered and treated with dilute sulphuric acid, whereby zinc is removed. The residue is heated to redness, and part of the base metals removed with dilute hydrochloric acid, and any gold dissolved out by further treatment with cold aqua regia.

The residue is heated in retorts with aqua regia, whereby most of the platinum passes into solution, together with some rhodium, osmium, palladium, and a little iridium, whilst the undissolved portion consists of osmiridium, ruthenium, and a little platinum. The solution is distilled, the osmium passing off as the volatile tetroxide, and the mother-liquor then neutralised with sodium carbonate. Addition of mercuric cyanide throws out the palladium as cyanide. Ammonium chloride added to the filtrate effects the precipitation of ammonium chlor-platinate and chlor-iridate. Ignition of these salts yields the spongy metal, which may be worked up as already indicated into the compact form.

If desired, the two ammonium salts may be separated prior to ignition, so that the pure metals may ultimately be isolated. This may be done conveniently by either of the following methods:

1. The salts are warmed gently with a solution of potassium cyanide. The ammonium chlor-iridate is reduced to chlor-iridite, which passes into solution, leaving the chlor-platinate as an insoluble residue.

2. The salts are suspended in water and sulphur dioxide passed through. The chlor-iridate is reduced to chlor-iridite and passes into solution, leaving the insoluble chlor-platinate as residue.

Ignition of the purified ammonium chlor-platinate yields a proportionately pure product of metallic platinum. The solution containing ammonium chlor-iridite may be evaporated to dryness and the residue ignited to yield metallic iridium.

Deville and Debray’s Method.—This method consists in melting the crude platinum, from which the gold has been removed, with excess of lead. On cooling, the mass is treated first with nitric acid, and then with aqua regia, whereby lead, platinum, and some rhodium pass into solution; iron, ruthenium, and rhodium remaining behind as a crystalline alloy. From the solution ammonium chlor-platinate is precipitated, and from it metallic platinum is prepared as described above.

This method is not now used.

A second method described by these authors consists in repeated melting of the crude platinum in a lime crucible, whereby volatile and oxidisable impurities are removed, the latter being absorbed by the
Platinum from Nickel Matte.—Platinum occurs in traces in the nickel ores of Sudbury (see p. 82), and is to some extent recovered from these in commercial practice by more or less secret processes. During the fiscal year ending March 31, 1916, the Canadian Copper Company produced 56,405 tons of nickel matte, the average sample of which contains:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>0.10 oz. (troy) per ton</td>
</tr>
<tr>
<td>Palladium</td>
<td>0.15 oz.</td>
</tr>
</tbody>
</table>

According to these figures, the 56,405 tons of matte contained:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>5640.5 oz. (troy)</td>
</tr>
<tr>
<td>Palladium</td>
<td>8461 oz.</td>
</tr>
</tbody>
</table>

The actual amount of these precious metals recovered during the year amounted to:

Palladium + platinum: 1098 oz. (troy)
Other platinum metals, mainly rhodium and iridium: 257 oz.

It will thus be seen that there is considerable opportunity of adding to the commercial supplies of the platinum metals from this source.

Preparation of Pure Platinum.—Commercial platinum usually contains some 2 per cent. of iridium, and for many purposes this is no disadvantage as the alloy is very durable and resistant to acid attack.

To obtain the pure metal several different processes may be adopted, all of which are complicated and require very careful handling if the last traces of rhodium, iridium, ruthenium, and iron are to be removed.

Matthey's Method.—Matthey recommends the following treatment for the commercial metal whereby it may be obtained in an exceptionally high state of purity. The platinum is melted with six times its weight of pure lead and, after granulation, treated with a mixture of nitric acid (1 part) and water (8 parts). When no more action is apparent the greater part of the lead will have dissolved out, together with a portion of any copper, iron, palladium, or rhodium that may have been present. The insoluble residue is in the form of an amorphous, black powder, and consists essentially of platinum, lead, iridium, and small proportions of the other metals originally present.

Digestion with dilute aqua regia effects the solution of the platinum and lead, leaving a residue of impure iridium. The solution is filtered, evaporated, and the lead converted into sulphate by addition of sulphuric acid in requisite quantity. The platinic chloride is extracted with water, and ammonium chlor-platinate precipitated in the usual way with excess of ammonium chloride containing sodium chloride. The whole is heated to 80° C. and allowed to stand for several days, most of the rhodium remaining in solution and imparting to the liquid a rose-coloured hue.

The precipitated ammonium chlor-platinate is repeatedly washed with a saturated solution of ammonium chloride, and subsequently with dilute hydrochloric acid. It still contains small quantities of rhodium, however, as ammonium chlor-rhodate. The salt is mixed with potassium hydrogen sulphate to which a small quantity of ammonium

hydrogen sulphate has been added, and gradually heated to redness in a platinum dish. The ammonium chlor-platinate is thereby reduced to platinum sponge, whilst the rhodium remains in a soluble state as a double sulphate with potassium.

The product is digested with water at the boiling-point, leaving a residue of platinum sponge in a high state of purity.

In addition to the rhodium sulphate the water will have extracted a small quantity of platinum in the form of sulphate.

Upon evaporating the solution to dryness and heating to redness the platinum sulphate is reduced to the metallic condition, the rhodium salt being unaffected. Digestion with water leaves a residue of pure platinum which may be added to the previous residue.

The metal thus prepared is very pure, and may, if desired, be worked into the compact form by the methods already detailed.

**Physical Properties.**—Platinum is a silver-white metal, capable of taking a high polish. It is slightly harder than silver, however, and does not tarnish. It is both malleable and ductile, admitting of being beaten out into thin foil and drawn into fine wire. Addition of a small quantity of iridium increases the hardness of the metal, but decreases its ductility.

Platinum is hardened by mechanical treatment, but is softened again on maintaining at bright red heat for several minutes.

The density of native platinum varies from 14 to 19, the variation being mainly due to impurities such as iron which may range from 5 to 16 per cent., and to smaller quantities of copper, iridium, osmium, rhodium, and palladium.

The density of pure platinum varies according to its physical condition, as is evident from the accompanying data which give the density calculated for a vacuum at 4° C.:

(1) Annealed pure platinum wire . . . 21.4403
Same wire cold drawn, not annealed . . 21.4336
(2) Annealed pure platinum wire . . . 21.4312
Same wire twisted, not annealed . . . 21.3985

The mean coefficient of linear expansion of platinum with rise of temperature between 0° and 1000° C. is 2:

\[ \alpha = 0.0000105t. \]

For temperatures ranging from 0° to 100° C.:

\[ \alpha = 0.0000089t. \]

These values are not far removed from those observed for different kinds of glass. Thus, for temperatures round and about 20° C. the following values have been obtained 3:

<table>
<thead>
<tr>
<th>Material</th>
<th>Coefficient of Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft glass</td>
<td>0.0000085</td>
</tr>
<tr>
<td>Hard glass</td>
<td>0.0000097</td>
</tr>
<tr>
<td>Flint glass</td>
<td>0.0000078</td>
</tr>
</tbody>
</table>

For this reason platinum wire is used in the construction of electrical and other apparatus in which it is necessary to pass wire through glass.

---


---

See Kaye and Laby, *Physical and Chemical Constants* (Longmans, 1911).
PLATINUM AND ITS COMPOUNDS

and leave a perfectly air-tight and hermetically sealed joint. Electric-light bulbs are an important example of this.

The specific heat of platinum between 0° and 100° C. has the mean value of 0.0323.

The heat liberated by one gram of platinum in cooling from \( t^o \) to \( t_o \) is given by the expression:

\[
\text{Quantity of heat} = 0.031590 (t - t_o) + 0.029234 (t^2 - t_o^2);
\]

and the specific heat at any temperature \( t \) is given by:

\[
\text{Specific heat} = 0.031590 + 0.029234 t.
\]

It will be observed that the specific heat of the metal rises with the temperature, and experiment shows that this is the case also at very high temperatures such as those of the incandescent metal, although theory would require its constancy under these latter conditions.

The melting-point of platinum has been variously given, the most recent results being 1759° C., and 1755° C. For other data the reader is referred to the references given below. The lowest temperature at which the volatilisation of platinum can be detected in a complete vacuum is given by Knocke as 540° C.

The most intense lines in the arc and spark spectra of platinum are as follow:

\[
\begin{align*}
\text{Arc:} & \quad 2659-60, \quad 2702-50, \quad 2705-99, \quad 2719-12, \quad 2830-40, \quad 2929-90, \quad 2998-07, \quad 3042-75, \quad 3064-82, \quad 3408-27, \quad 4412-75, \quad 4498-93, \quad 4521-10. \\
\text{Spark:} & \quad 2424-90, \quad 2659-58, \quad 2998-08, \quad 3064-82, \quad 3923-15, \quad 4118-83, \quad 4498-90, \quad 4552-60.
\end{align*}
\]

Volatilisation of Platinum.—When platinum apparatus is heated to very high temperatures it frequently undergoes a marked alteration in weight, becoming lighter. This is generally attributed to volatilisation of the metal, and several useful investigations have recently been carried out with the object of determining how the loss may best be avoided.

1 Magnus, Ann. Physik, 1916, [iv], 48, 983. Other expressions have been given, namely:

\[
\text{Specific heat} = 0.03198 + 0.034 t
\]

(White, Amer. J. Sci., 1909, [iv], 28, 334);

\[
\text{Specific heat between } 0^o \text{ and } 300^o \text{ C.} = 0.030456 + 0.02972 t + 0.005611 t^2
\]

2 Schlett, Ann. Physik, 1908, [iv], 26, 201). The data given by Regnault, Dulong and Petit, Violle, etc., are now of historical interest only.

3 Waidner and Burgess, Bureau of Standards, Washington, 1907, 3, 163.

4 Day, Trans. Faraday Soc., 1911, 7, 136. Féry and Chéneveau (Compt. rend., 1909, 148, 401) suggest that the melting-point of the metal, like that of silver, is influenced by the nature of the atmosphere in which fusion takes place, but Waidner and Burgess (ibid., p. 1177) do not accept the explanation.


7 Exner and Haschek, Die Spektren der Elemente bei normalem Druck (Leipzig and Wien, 1911).

8 For earlier reports on this subject, see Wittstern, Dingler's Poly. J., 1866, 179, 299; Stolza, ibid., 1870, 198, 177; Eilers, J. prakt. Chem., 1866, [i], 99, 257; de Koninck,
Although it is generally assumed that the loss in weight of pure platinum on heating is due to direct volatilisation of the metal, Roberts points out that this is improbable since platinum does not volatilise in nitrogen, hydrogen, or in vacuo. He determined the lowest temperatures at which platinum volatilises in oxygen by an exceedingly sensitive method, namely, by sudden expansion of gas saturated with moisture, which when any volatilisation has taken place results in the formation of a cloud or mist, because the disintegrated particles constitute condensation nuclei. It was found that platinum begins to disintegrate at 500° C., the extent of volatilisation being roughly proportional to the oxygen pressure. Roberts therefore concludes that the phenomenon is due to the formation of platinum dioxide, PtO₂, which is endothermic and which dissociates at lower temperatures.

Crookes had in 1911 already studied the relative volatilities of the metals of the platinum group at temperatures ranging from 900° C. upwards. The metals were heated in still air in an Heraeus furnace, the order of volatilisation proving to be as follows: Ru, Ir, Pd, Pt, and Rh, the last named being the least volatile.

Burgess and Sale show that the presence of iridium in the platinum of crucibles, although added for its stiffening qualities, renders the latter subject to proportionately greater losses of weight on heating to temperatures above 900° C. Below this temperature, and up to a content of at least 3 per cent. of iridium, the loss on heating is negligible. Below 900° C. also the presence of rhodium and silicon has a negligible effect. The presence of iron appears to lower the heat losses by amounts depending on the quantity of that metal present. Below 900° C. there may even be a slight gain in weight on heating platinum owing to the iron content diffusing to the surface and oxidising. This is a decided disadvantage, however, on account of the solubility of the iron oxide in acids.

Rhodium, like iridium, stiffens platinum; but unlike iridium it reduces the volatilisation of platinum at all temperatures above 900° C. It is suggested, therefore, that a useful alloy for best quality crucibles "would be platinum containing 3 to 5 per cent. of rhodium, practically free from iron and iridium, and containing no other detectable impurities."

Diffusion of Gases through Platinum.—Hydrogen diffuses through heated platinum, but less rapidly than Graham's experiments would suggest. Methane, despite its low density, does not diffuse through heated platinum, neither do oxygen, nitrogen, argon, and helium. The diffusion of hydrogen through platinum has been studied by many investigators, notably by Winkelmann, who shows that its rate


5 Burgess and Sale, opus cit., p. 311.

6 Randall, Amer. Chem. J., 1897, 19, 682.


8 Winkelmann, Ann. Physik, 1902, [iv], 8, 388.
increases after the platinum has been heated for some time, in consequence of the crystalline structure assumed by the metal. The diffusion of hydrogen through platinum at red heat is not directly proportional to the pressure of the gas. Probably this is due to the diffusion being accompanied by dissociation of the hydrogen molecules, the atoms, only, of the hydrogen passing through the metal (see p. 177).

**Solubility of Gases in Platinum.**—The solubility of hydrogen in platinum has been studied by Sieverts, who has shown that the gas is less soluble in compact platinum than in the same weight of iron or nickel. At constant pressure the solubility rises with the temperature, whilst at constant temperature the amount of hydrogen absorbed is directly proportional to the square root of the pressure. On cooling, all the hydrogen absorbed at higher temperatures by the metal is evolved.

Platinum does not absorb carbon dioxide or sulphur dioxide.

Platinum which has been heated to a high temperature in a current of hydrogen is usually found to have undergone a slight permanent change, its melting-point being depressed and its ductility reduced. This, however, appears to be due to the absorption of small quantities of carbon from traces of organic impurity in the hydrogen, and not to the influence of the pure hydrogen itself.

**Chemical Properties.**—Platinum is one of the most permanent of metals, remaining untarnished in air at high and low temperatures, even in the presence of moisture. It is attacked both by fluorine and by chlorine when heated in these gases; in fluorine at 500° to 600° C., yielding the tetrafluoride, and if in the form of sponge, in chlorine at about 350° C., yielding the dichloride.

When heated in a current of chlorine at about 1400° C. platinum apparently volatilises, condensing on cooler parts of the apparatus in crystalline form. This is attributable to the formation of a volatile chloride.

When heated in dry oxygen, either in the form of thin foil or as sponge, it becomes superficially blackened in consequence of oxidation to the monoxide, PtO. This compound, however, decomposes at higher temperatures.

Platinum is very slowly attacked by hot concentrated sulphuric acid, particularly at about 250° to 280° C., but the introduction of sulphur dioxide into the liquid, by addition of a piece of sulphur or carbon, completely prevents the solution of the metal. Carbon dioxide and nitrogen are without influence, but arsenious and antimonious oxides exert a marked protective effect upon the metal. It is suggested that in the case of the pure acid, dissociation of sulphur trioxide into dioxide and oxygen takes place, the last named attacking the platinum. The sulphur dioxide, when added from an external source, owes its protective influence to the fact that it represses the dissociation, whilst the arsenious and antimonious oxides act by absorbing the oxygen.

In attacking platinum with sulphuric acid, the presence of oxygen,
although facilitating solution of the platinum, is not absolutely essential. The oxygen plays a secondary part in that it modifies the equilibrium of the initial action of the acid upon the metal, as represented by the equation:

\[ 2\text{Pt} + 7\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{Pt(OH)(HSO}_4\text{)}_2 + 3\text{SO}_2 + 4\text{H}_2\text{O}, \]

the reaction being regarded as reversible.

From the solution obtained by dissolving platinum in concentrated sulphuric acid two substances have been isolated, namely, a yellow hydroxyhydrogen sulphate, Pt(OH)(HSO\textsubscript{4})\textsubscript{2}, and a reddish brown compound, the composition of which is probably represented by the formula Pt(OH)(HSO\textsubscript{4})(H\textsubscript{2}O). This last-named substance is only formed after prolonged boiling of platinum with concentrated acid for some twenty hours. It crystallises in rectangular prisms, which are very soluble in water, in concentrated sulphuric acid, and also in alcohol.

Dilute sulphuric acid does not attack platinum, not even if hydrogen peroxide is added; neither does a mixture of glacial acetic acid and hydrogen peroxide.\(^2\)

Nitric acid is without action on pure platinum, and the hot concentrated acid should extract practically nothing from a well-cleaned crucible of the pure metal.\(^3\)

When alloyed with certain other metals such as silver, for example, platinum dissolves to a considerable extent in nitric acid (see p. 281).

Aqua regia dissolves platinum with ease, yielding the hexachloroplatinic acid. This is mainly due to the chlorine liberated, since boiling hydrochloric acid, like boiling nitric acid, alone is without action on the metal.

As a solvent for platinum a mixture of concentrated hydrochloric acid with chloric acid has been recommended,\(^4\) its activity being due to the chlorine liberated by the interaction:

\[ 5\text{HCl} + \text{HClO}_3 = 3\text{Cl}_2 + 3\text{H}_2\text{O}. \]

Platinum is slightly attacked by fused alkali carbonate, more so by the fused nitrate or hydrogen sulphate, and strongly attacked by fused hydroxide or peroxide.

When platinum wire is heated in ammonia gas at 800°C, its surface becomes dull, and shows a more or less blistered appearance under the microscope. A fine deposit of platinum black also gradually collects on the surface of the metal due to disintegration of the compact platinum.\(^5\)

When platinum is heated in a luminous coal-gas flame a black layer is formed. If the carbon is now burnt off in air the metal is left in a rough and brittle condition, but without having undergone any loss in weight. The action is considerably enhanced by the presence of alloyed rhodium or iron, whilst iridium has a less marked effect.\(^6\)

In the case of pure platinum the action is due to the presence of carbon disulphide in the coal gas.\(^7\)

---

A mixture of methane, ethylene, carbon monoxide, and hydrogen is without action upon the pure metal, although commercial platinum is blackened by it.

When heated in direct contact with different forms of carbonaceous material such as coal, coke, charcoal, etc., platinum is liable to become brittle and to fracture easily.¹

At 1600° C. platinum effects the reduction of both ferric oxide and ferrosferric oxide in air, oxygen being evolved and a solid solution of iron in platinum remaining as residue. The same reaction obtains at lower temperatures, namely, at 1200° C., if the oxygen pressure is very small. This explains why platinum crucibles sometimes increase in weight when used to heat oxides of iron at high temperatures.²

Sulphur alone has no action upon platinum,³ but metallic sulphides are liable to attack it. Phosphorus, phosphides, and phosphates under reducing conditions attack the metal, so that these and the aforesaid sulphides should not be ignited in platinum crucibles in quantitative analysis. Ferric chloride solution is reduced to ferrous chloride when evaporated in a platinum dish, platinum passing into solution.

When plates of platinum are kept in an alkaline solution of potassium permanganate for some twenty-four hours at the ordinary temperature they become superficially attacked, and on treatment with dilute potassium iodide solution and hydrochloric acid, red solutions are obtained, from which platinum sulphide may be precipitated on passage of hydrogen sulphide.⁴

Platinum readily alloys with many metals. The ease with which it alloys with lead is a property made use of in assaying the metal.

**Solder for Platinum.**—The only suitable solder for platinum and iridio-platinum is pure metallic gold.

**Platinum Plating.**—A pure white deposit of platinum may be obtained by using a boiling solution consisting of:

- 4 grams platinum tetrachloride,
- 20 grams ammonium phosphate,
- 90 grams sodium phosphate, and
- 5 grams sodium chloride

per litre. The article to be plated should be kept in motion, and a potential difference of from 6 to 8 volts maintained.⁵

**Catalytic Activity.**—Platinum possesses considerable catalytic activity, even in the compact state, for thin platinum foil or wire when freshly heated in air glows upon insertion in a current of coal gas, and causes ignition if a jet of hydrogen gas is allowed to impinge upon it.

But it is when platinum is in a finely divided condition that its catalytic activities are most pronounced.

That in such circumstances the metal can act catalytically in assisting chemical reactions to take place has been known for many

---


⁴ Marie, *Compt. rend.*, 1908, 145, 475.

years. Thus the reduction of nitric oxide to ammonia by means of hydrogen in the presence of platinum was observed by Kuhlmann in 1888; the combination of iodine with hydrogen, by Corewinder in 1852; the conversion of hydrocyanic acid into methylamine, by Debus in 1862; and the production of ethane from acetylene, by de Wilde in 1874.

It is frequently convenient to employ finely divided platinum in the form of a deposit upon other substances such as asbestos.

Paal and Windisch ¹ prepared platinised metals such as nickel, copper, etc., by shaking the metal in the form of powder with an aqueous solution of chlor-platinic acid, a deposit of platinum amounting to about 2-5 per cent. of the weight of the base metal being aimed at. The product was washed with water, alcohol, and ether, in succession, and dried in vacuo.

It was found that nickel has no effect upon the catalytic activity of the platinum; aluminium, cobalt, and bismuth reduce its activity appreciably; whilst copper, zinc, silver, tin, and iron inhibit its activity altogether.

Platinised asbestos has been used to catalytically accelerate many chemical reactions, such as, for example, the union of oxygen and sulphur dioxide to form the trioxide. This reaction proceeds almost to completion in presence of excess of air, and in 1898 and 1899 several patents were issued in respect of this process.²

Dilute solutions of potassium permanganate are reduced by finely divided platinum, potassium hydroxide and hydrated manganese dioxide being produced. Thus ³:

\[
2\text{KMnO}_4 + \text{H}_2\text{O} = 2\text{KOH} + \text{Mn}_3\text{O}_7 \\
\text{Mn}_3\text{O}_7 + 4\text{H}_2\text{O} = 2\text{Mn} (\text{OH})_4 + 3\text{O}.
\]

In a similar manner the reduction or hydrogenation of numerous organic substances such as cinnamic acids, etc., has been effected with finely divided platinum.⁴

**Passivity.**—It is now a matter of common knowledge that platinum, like iron, cobalt, and nickel, exhibits passivity under certain conditions.⁵ Possibly this is due to the formation of a superficial layer of oxide which protects the underlying metal from attack. This explanation is supported by the fact that during the electrolysis of platinum chloride solution with platinum electrodes, the anode becomes slightly coated with oxide,⁶ and the same is true when dilute sulphuric acid containing from 2-5 to 10 per cent. of acid is similarly electrolysed.⁷

The coating of oxide formed is yellow to brown in colour, and is insoluble in cold sulphuric acid alone, although it dissolves in the presence of a reducing agent. It is not formed, however, in 50 per

¹ Paal and Windisch, *Ber.*, 1913, 46, 4010.
² See account by Knetsch, *Ber.*, 1901, 34, 4069. Also this Series, Vol. VII.
cent. sulphuric acid, being apparently soluble in that concentration of acid. Its possible formation, therefore, can hardly be offered as an explanation for the insolubility of platinum in the more concentrated acid. If, therefore, in the latter case an oxide film is formed during electrolysis, it would appear that a different oxide must be postulated from that produced in dilute solution.\(^1\) What the compositions of such oxides may be is uncertain. Possibly the trioxide, PtO\(_3\), is not altogether unconnected with these phenomena.\(^2\)

**Crystalline Platinum.**—Moissan\(^3\) observed that on decomposing platinum tetrafluoride at a high temperature the metal was left as a distinctly crystalline residue. This was indirectly confirmed by Joly,\(^4\) who passed an electric current through pure platinum ribbon dusted over with finely divided topaz. After being maintained at red heat for half an hour microscopic crystals of platinum could be observed clinging to partially decomposed topaz. These gradually increased in size, some reaching 0.1 mm. in the course of two hours. The crystals possessed a high metallic lustre, and belonged to the cubic system, the prevailing form being the octahedron or some modification of it. They were unattacked by hot hydrochloric, sulphuric, or nitric acid, and appeared to be unaffected by cold hydrofluoric acid, although slightly attacked by the last named when hot. Boiling aqua regia completely dissolved the crystals. It is not improbable that fluorine, liberated from the topaz at the high temperature, attacked the platinum, yielding the fluoride which in turn dissociated, leaving the residue of crystalline metal.

Crystalline platinum may also be obtained by ignition of potassium chlor-platinate,\(^5\) and by heating spongy platinum with cupric chloride.\(^6\) Small crystals have been observed in electric furnaces near to platinum electrodes, evidently due to the sublimation of the metal below its melting-point.\(^7\)

**Platinum Hydrosol or Colloidal Platinum.**—A solution of platinum hydrosol or colloidal platinum in water is easily prepared by sparking between platinum electrodes immersed in ice-cooled water,\(^8\) a current of about 10 amperes and 40 volts being employed. The electrodes consist of thick platinum wire, and, when placed from 1 to 2 mm. apart, sparking takes place, particles of the metal being torn off and suspended in the water. The liquid thus obtained is allowed to stand overnight, and decanted from any sediment. It has a dark colour, but the individual metallic particles cannot be distinguished even with the aid of a microscope.

Colloidal platinum may also be prepared by reduction of the chloride with hydrazine hydrate, in the presence of a protective colloid (vide infra).

Castoro recommends acraldehyde as a suitable reducing agent.\(^9\)

When platinum wire is heated to incandescence and plunged into

---

\(^1\) Ruer, _loc. cit._, p. 633.
\(^2\) Wöhler and Martin, _Ber._, 1909, 42, 3326.
\(^3\) Moissan, _Compt. rend._, 1889, 109, 897.
\(^4\) Joly, _Nature_, 1891, 43, 541.
\(^7\) Guntz and Bassett, jun., _Bull. Soc. chim._, 1905, [ii], 33, 1306.
\(^8\) Bredig and vom Berneck, _Zeitch. physikal. Chem._, 1899, 31, 258.
\(^9\) Castoro, _Zeitch. anorg. Chem._, 1904, 41, 126.
distilled water the presence of colloidal metallic particles can be detected by ultra-microscopic examination.¹

As mentioned above, the stability of colloidal metal solutions is considerably enhanced by the addition of certain organic substances or protective colloids. For example, gelatin has been frequently employed, 0·5 gram per litre of colloidal solution proving very effective in preventing the coagulation or precipitation of the metal.² Extracts of Iceland moss ³ and of quince seed ⁴ have also been recommended.

Paal² employs the sodium salts of protalbinic and lysalbinic acids, which are prepared from egg albumen by heating at 100° C. with a 8 per cent. solution of sodium hydroxide. Addition of acetic acid effects the precipitation of protalbinic acid, which is washed free from salts by dialysis. The mother-liquors contain lysalbinic acid, which is separated by concentrating to small bulk and acidifying with sulphuric acid. It may be purified by dissolving in water and pouring the solution into alcohol. An alkaline solution of either of these acids is prepared, and to it a solution of platinitic chloride is added and a slight excess of hydrazine hydrate, the whole being allowed to stand for five hours. The salts produced are washed away by dialysis and the colloidal solution concentrated, the product being dried at 105° C., when it yields black scales, readily soluble in water to a brown opalescent solution.

Amberger ⁶ has used lanolin as protective colloid. The lanolin is impregnated with an aqueous solution of a platinitous salt, and intimately mixed with the requisite quantity of alkali hydroxide to precipitate out the platinum as hydrated oxide. This is reduced to colloidal metallic platinum by hydrazine hydrate. Both the lanolin and the colloidal metal are dissolved by light petroleum or chloroform, and the whole of the metal with a portion of the lanolin may be re-precipitated on addition of alcohol—a reaction affording a means of increasing the concentration of the metal in the preparation.

When stannous chloride is added to solutions of platinum salts a red coloration is produced, which is due to the formation of so-called red colloidal platinum, which is kept in a fine state of division by the colloidal products of hydrolysis of the stannous chloride.⁷ In the absence of a protective colloid the red platinum changes to brown colloidal platinum. An interesting analogy may be traced between this red colloidal metal and the better-known colloidal gold, termed “purple of Cassius.”

Colloidal platinum possesses considerable catalytic activity. For example, it stimulates the decomposition of hydrogen peroxide solution, a dilution of one gram atom of platinum in 70 million litres of water having a pronounced accelerating effect.

The decomposition of hydrogen peroxide in this manner is a con-

³ Gutbier and his collaborators, Kolloid-Zeitsch., 1916, 18, 87.  
⁴ Gutbier and Wagner, ibid., 1916, 19, 298.  
⁵ Paal, Ber., 1914, 47, 2202.  
⁶ Amberger, Kolloid-Zeitsch., 1913, 13, 310, 313.  
venient reaction to study, since its rate can be followed by titration with potassium permanganate. Both in acid and in neutral solution it proceeds strictly in accordance with the monomolecular reaction:

$$H_2O_2 = H_2O + O.$$  

In alkaline solution the catalytic action of the colloidal platinum increases to a maximum with increase of alkali concentration and then decreases, in which respect it behaves in a precisely similar manner to certain organic ferments.

Colloidal platinum still further resembles organic ferments in its action upon hydrogen peroxide in that its activity is reduced or partially paralysed by the addition of poisons such as hydrogen cyanide, hydrogen sulphide, or mercuric chloride. After a time, however, the metal may recover from these.

The reaction is not affected by light, but increases with the concentration of the platinum, although not directly in proportion to the same; it is also enhanced by rise of temperature.\(^1\)

The rate of decomposition of hydrogen peroxide by colloidal platinum has been made use of in determining the absolute and relative influences of different protective colloids upon the colloidal metal,\(^2\) the times required for the decomposition of a definite percentage of the peroxide under varying conditions being noted.

With gelatin the results are typical, and are given in the following table:

<table>
<thead>
<tr>
<th>Percentage of Gelatin</th>
<th>Relative Times required to decompose 50 per cent. of the Peroxide Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>100</td>
</tr>
<tr>
<td>0.001</td>
<td>437</td>
</tr>
<tr>
<td>0.01</td>
<td>460</td>
</tr>
<tr>
<td>0.05</td>
<td>620</td>
</tr>
<tr>
<td>0.10</td>
<td>983</td>
</tr>
</tbody>
</table>

It will be observed that even small quantities of gelatin exert a most important influence, retarding the decomposition of the peroxide very considerably, as is usual with a protective colloid. The gelatin, however, increases the stability of the colloidal metal solution, and tends to prolong its period of activity by preventing its precipitation by electrolytes, thereby enabling many reactions to be studied other than the decomposition of pure hydrogen peroxide solution.

When colloidal platinum is added to mixtures of Caro's permonosulphuric acid and aqueous hydrogen peroxide, oxygen is rapidly evolved; thus \(^3\):

$$H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2.$$  

Solutions of hydrogen peroxide and potassium persulphate interact slowly in the cold, the rate of reaction being greatly enhanced by the addition of colloidal platinum \(^4\):

$$K_2S_2O_8 + H_2O_2 = K_2SO_4 + H_2SO_4 + O_2.$$  

\(^2\) Groh, *ibid.*, 1914, 88, 414.  
\(^4\) Friend, *ibid.*, 1906, 89, 1082.
Carbon monoxide combines with oxygen to yield carbon dioxide when shaken at ordinary temperatures with colloidal platinum solution,\(^1\) whilst hydrogen and oxygen gases unite under similar conditions to yield water.\(^2\)

Colloidal platinum solution absorbs hydrogen gas, a rough proportionality existing between the concentration of the metal and the volume of hydrogen absorbed. Certain protective colloids, such as gum acacia, dextrin, and albumen, tend to reduce the amount of hydrogen absorbed, but sucrose has a negligible effect.\(^3\) It was to be expected, therefore, that colloidal platinum would assist in the reduction of many substances in the presence of hydrogen gas. This has, indeed, proved to be the case. Acetylene is reduced to ethylene and ethane,\(^4\) and ethylene is reduced to ethane.\(^5\) The activity of the metal diminishes after repeated use, and, just as in the decomposition of peroxide already referred to, the reactions are increased by increasing the concentration of the colloidal metal, such increase is by no means directly proportional to the concentrations employed.

Ferric salts are reduced to ferrous,\(^6\) and ammonium molybdate likewise suffers reduction.\(^7\)

Platinum hydrosol also catalytically assists in the reduction or hydrogenation of many organic substances such as unsaturated oils. To this end an aqueous solution of colloidal platinum is added to an alcoholic solution of the organic substance and hydrogen gas bubbled through. The temperature, pressure, and extent of agitation of the liquid are important factors. In this manner linseed and other oils are readily reduced, saturated or "hardened," to yield white fatty substances.\(^8\)

The activity of colloidal platinum is reduced by such poisons as hydrogen cyanide or sulphide,\(^9\) but increased by short exposure to ultra-violet light. On the other hand, prolonged exposure to ultra-violet light causes the deposition of the metal as a black, flocculent precipitate, its catalytic activity being thereby totally destroyed.\(^10\)

Colloidal platinum may also be coagulated by introducing plates of various metals into its aqueous solutions. It is found that plates with roughened surfaces are more active than those that are smooth, other things being equal. The following is the order of activity of the five metals that have been experimented with, the first named causing the most rapid coagulation of the platinum, and the last named the slowest: zinc, steel, nickel, tin, and copper.\(^11\) The explanation appears to lie in the solution of traces of the metals upon introduction into the colloidal solution, whereby positively charged ions are formed which neutralise the negative charges of the colloid particles. In support of

\(^{1}\) Paal, \textit{Ber.}, 1910, 49, 548.
\(^{2}\) See Paal and Schwarz, \textit{J. prakt. Chem.}, 1916, [ii], 93, 106.
\(^{4}\) Paal and Schwarz, \textit{Ber.}, 1915, 48, 1202.
\(^{5}\) Paal and Schwarz, \textit{ibid.}, p. 994.
\(^{6}\) Eggert, \textit{Zeitsch. Elektrochem.}, 1914, 20, 370; 1915, 21, 349.
\(^{7}\) Paal and Büttnner, \textit{Ber.}, 1915, 48, 220.
\(^{8}\) Numerous other examples of reduction, mainly of organic substances, have been investigated. Paal and Gerum, \textit{Ber.}, 1908, 41, 2273.
\(^{9}\) Bredig and Ikeda, \textit{ibid.}, 1901, 31, 1; Price and Friend, \textit{Trans. Chem. Soc.}, 1904, 85, 1526.
this, it is interesting to note that the presence of copper has been demonstrated in the coagulated mass precipitated from colloidal solution by the introduction of a copper plate.

**Solid Platinum Hydrosol.**—The hydrosol may be obtained in the solid state, completely soluble in warm water. This is most readily accomplished by concentration over sulphuric acid *in vacuo* of the colloidal solution obtained by reducing a platinum salt with hydrazine hydrate in the presence of a protective colloid, such as gum acacia.

**Platinum Black.**—This consists of platinum in a very fine state of division, and contaminated with traces of foreign substances which vary according to its method of preparation. This usually consists of precipitating the metal from solutions of its salts by reducing agents. To this end alcohol has been used successfully in the presence in alkalies; sodium formate, glucose in alkaline solution, sodium acetate, hydrazine hydrate in alkaline solution, formaldehyde in sodium hydroxide solution, and glycerine with potassium hydroxide have also been used as reducing agents. Instead of these reagents, the more highly electropositive metals may be used, as, for example, magnesium, zinc, or aluminium. The last-named metal is recommended by McDermott in sheet form for the reduction of platinum chloride solution since the precipitated platinum is relatively pure, very finely divided, and contains no aluminium, whereas, when zinc is used, traces of this metal contaminate the precipitate.

Platinum black is a powerful catalyst, effecting the union of hydrogen and oxygen with explosive violence. It readily absorbs hydrogen. Although the hydrosol of platinum enables carbon monoxide to unite with oxygen to form the dioxide when shaken with the mixed gases at ordinary temperatures, this reaction does not appear to take place in the presence of platinum black.

An interesting reaction consists in the oxidation of atmospheric nitrogen in air by the agency of platinum black in the presence of potash or baryta water, whereby nitrous acid or ammonium nitrite are produced.

Not only are oxidising reactions accelerated by platinum black, but reductions are similarly hastened. In the presence of dextrose it reduces free nitric acid to ammonia, potassium chlorate and perchlorate to chloride, and potassium iodate to iodide. By heating platinum black to between 300° and 500° C. its catalytic hydrogenation activity is appreciably reduced.

---

1 Gutbier and Hofmeier, *J. prakt. Chem.*, 1905, [ii], 358.
Hydrazine hydrate is converted by platinum black into free nitrogen and ammonia,\(^1\) the reaction proceeding according to the equation:
\[
3\text{N}_2\text{H}_4\cdot\text{H}_2\text{O} = 4\text{NH}_3 + \text{N}_2 + 3\text{H}_2\text{O}.
\]

Neither hydrogen nor nitrous oxide appears to be formed during the process.

Platinum black slowly absorbs 60 times its volume of carbon monoxide at ordinary temperature, and appears to form a chemical compound with it, although efforts to isolate any such substance have hitherto proved abortive. The absorption can hardly be a purely mechanical effect, since other gases such as hydrogen do not affect its elimination. Upon heating to \(250^\circ\text{C}\), the carbon monoxide is suddenly liberated.\(^2\)

Platinum black, if it has not been ignited, dissolves in concentrated hydrochloric acid in the presence of hydrogen peroxide, yielding chlorplatinate, \(\text{H}_2\text{PtCl}_6\), which, from its method of preparation, is entirely free from nitro compounds.\(^3\)

When exposed to red heat, platinum black shrinks and becomes spongy, no longer blackening the fingers.

**Platinum Sponge** is obtained by igniting ammonium chlorplatinate, preferably in hydrogen, when metallic platinum is left behind as a dull, grey, soft and porous mass. Its density is approximately \(21.16\).\(^4\)

When heated to whiteness it may be welded by hammering into compact platinum foil.

Platinum sponge readily absorbs hydrogen, and when charged with this gas becomes incandescent in air owing to the induced combustion. This is the principle of the Doebereiner Lighter used for igniting coal gas without a match. Hydrogen and chlorine readily unite in the presence of platinum sponge, as also do hydrogen and iodine, although not quite so rapidly. Platinum sponge prepared at a relatively low temperature will cause hydrogen and oxygen to unite with explosive violence.

When spongy platinum or even the compact foil is boiled with sulphuric acid containing ammonium sulphate, sulphur dioxide is formed, and some free nitrogen evolved. The platinum apparently acts as a catalyst by alternately yielding the disulphate and free metal, thus:
\[
\text{Pt} + 4\text{H}_2\text{SO}_4 = \text{Pt(SO}_4)_2 + 2\text{SO}_2 + 4\text{H}_2\text{O}
\]
\[
3\text{Pt(SO}_4)_2 + 2(\text{NH}_3)_2\text{SO}_4 = 2\text{N}_2 + 3\text{Pt} + 8\text{H}_2\text{O} + 8\text{SO}_2.
\]

Nitrogen is not evolved if the platinum is replaced by gold or iridium.\(^5\)

**Explosive Platinum** is obtained by dissolving an alloy of the metal with excess of zinc in hydrochloric acid. The zinc passes into solution, leaving metallic platinum in the form of a finely divided residue. As obtained in this way the platinum is frequently explosive, but not always; its behaviour is very erratic in this respect.

The explosive property appears to be due to the union of occluded

---


\(^5\) Delépine, *Compt. rend.*, 1905, 141, 886.
PLATINUM AND ITS COMPOUNDS 275

oxygen and hydrogen, for the metal is not explosive if obtained in the entire absence of air.  

Atomic Weight.—*Approximate Value.*—Several lines of argument lead us to the conclusion that the atomic weight of platinum is approximately 195, and not a multiple or submultiple of this amount. The more important of these may be summarised as follows:

1. The specific heat of platinum between 0° and 100° C. is 0.0823. Assuming a mean atomic heat of 6.4, application of Dulong and Petit’s Law leads to the value 198 for the approximate atomic weight of platinum.

2. The chemical properties of platinum and its compounds exhibit interesting resemblances with those of nickel and palladium, on the one hand, and, on the other, they serve to complete the gradation in properties observable as we pass from osmium through iridium to platinum. There can thus be only one position for the metal in the Periodic Scheme, namely, at the close of the third vertical column in Group VIII, and with an atomic weight slightly greater than 193.1 (at. wt. of iridium).

3. The measurements made by Zambonini of the crystalline potassium salts of plumbic, stannic, and platinic acids shows that the salts are isomorphous. By Mitscherlich’s Law, therefore, they should have a similar constitution, and assuming the first two salts to be represented by the formulae K₃Pb(OH)₆ and K₂Sn(OH)₆ respectively, it follows that the platinate has the formula K₂Pt(OH)₆. In other words, a molecule of potassium platinate contains one complete atom of platinum, and one only. Similarly potassium chlor-platinate is isomorphous with potassium chlor-stannate, K₂SnCl₆, and may be assumed to have the formula K₂PtCl₆. Analysis of these compounds indicates, therefore, that the atomic weight of platinum is 195.2 and not a multiple or simple fraction of this amount.

Exact Value.—The first determination of the atomic weight of platinum was made by Berzelius in 1826. From the analysis of platinous chloride he found Pt = 194.7. Two years later he published his determination of the composition of potassium chlor-platinate; 6.981 parts of the salt lost 2.024 of chlorine when ignited in hydrogen, leaving a residue containing 2.822 of platinum and 2.135 of potassium chloride. Hence:

\[
\begin{align*}
\text{From } K₂PtCl₆ & : 4\text{Cl} & \text{Pt} = 198.3 \\
& \quad K₂PtCl₆ : 2\text{KCl} & \text{Pt} = 196.6 \\
& \quad K₂PtCl₆ : \text{Pt} & \text{Pt} = 197.4 \\
& \quad 2\text{KCl} : \text{Pt} & \text{Pt} = 197.1
\end{align*}
\]

These results are now known to be extremely high, but until 1881 the accepted figure for the atomic weight of platinum rested entirely upon them, and they appeared to be corroborated by some analyses published by Andrews in 1852.

In 1881 Seubert, by his analyses of ammonium and potassium chlor-platinate, showed that the atomic weight of platinum approaches the

\[\text{2 See Belluci and Parravano, *Atti R. Accad. Lincei*, 1905, [v], 14, ii, 457.}
\[\text{3 Berzelius, *Pogg. Annalen*, 1826, 8, 177.}
\[\text{4 Berzelius, *ibid.*, 1828, 13, 468.}
\[\text{5 Andrews, *British Association Report*, 1852.}
\[\text{6 Seubert, *Annalen*, 1881, 207, 1; *Ber.*, 1881, 14, 805.}
value $Pt = 195$, and not 197. His results were confirmed by Halberstadt in 1884, while Dittmar and McArthur three years later arrived at a somewhat higher figure as the result of four rather unsatisfactory analyses of potassium chlor-platinate.

The results of Seubert and Halberstadt have now been supplanted by the more modern work of Archibald, so that it will suffice to quote the ratios that they established and the values for the atomic weight of platinum deduced from them.³

**Seubert**

22 expts. $(NH_4)_2PtCl_4 : Pt = 100-000 : 43-953 \quad \text{whence } Pt = 195-13$

3 expts. $(NH_4)_2PtCl_6 : Pt = 100-000 : 51-864 : 100-000 \quad \text{, } Pt = 197-22$

8 expts. $K_2PtCl_4 : Pt = 100-000 : 40-107 \quad \text{, } Pt = 194-83$

8 expts. $K_2PtCl_6 : 2KCl = 100-000 : 80-682 \quad \text{, } Pt = 195-06$

3 expts. $K_2PtCl_6 : 4AgCl = 84-809 : 100-000 \quad \text{, } Pt = 195-31$

**Halberstadt**

10 expts. $PtBr_2 : Pt = 100-000 : 37-847 \quad \text{whence } Pt = 194-65$

82 expts. $(NH_4)_2PtBr_4 : Pt = 100-000 : 27-429 \quad \text{, } Pt = 194-87$

18 expts. $K_2PtBr_4 : Pt = 100-000 : 25-915 \quad \text{, } Pt = 195-08$

18 expts. $K_2PtBr_4 : 2KBr = 100-000 : 31-591 \quad \text{, } Pt = 195-78$

18 expts. $(NH_4)_2PtCl_6 : Pt = 100-000 : 43-943 \quad \text{, } Pt = 195-01$

19 expts. $K_2PtCl_6 : Pt = 100-000 : 40-098 \quad \text{, } Pt = 194-75$

19 expts. $K_2PtCl_6 : 2KCl = 100-000 : 80-663 \quad \text{, } Pt = 195-29$

The modern value for the atomic weight of platinum is based upon the extremely careful analyses of the chlor-platinates and brom-platinates of potassium and ammonium published by Archibald in 1909. The utmost precautions which modern experience has shown to be necessary were taken in preparing the salts in a state of purity and dryness, and in effecting the numerous analytical operations.

The analyses of potassium chlor-platinates were carried out in the following manner. The pure dry salt was weighed and heated in a stream of hydrogen:

$$K_2PtCl_6 + 2H_2 = 2KCl + Pt + 4HCl.$$  

The hydrogen chloride produced was absorbed in water and the hydrogen chloride in the solution determined by titration against a weighed amount of silver, dissolved in nitric acid, the end point being determined nephelometrically.⁵ The precise silver equivalent of the hydrogen chloride having been thus determined, the silver chloride produced was collected, washed, dried, and weighed. The residual mixture of potassium chloride and platinum was treated with water to wash out the potassium salt, and the platinum collected, heated in hydrogen, cooled, and weighed. The chlorine in the potassium chloride

¹ Halberstadt, Ber., 1884, 17, 2922.
³ These and all succeeding values are not those to be found in the original memoirs, but have been recalculated, employing the following antecedent data:

$$O = 16-000, \quad H = 1-00762, \quad N = 14-008, \quad Cl = 35-457, \quad Br = 79-916, \quad K = 39-100, \quad Ag = 107-880.$$

⁵ See this Series, Vol. I, p. 246.
was determined first by titrating it against silver, and then by collecting and weighing the silver chloride produced in that operation. Thus, corresponding to a certain weight of potassium chlor-platinate, there were obtained two weights of silver, two weights of silver chloride, and one weight of platinum, the six weights being in the following proportions:

\[ \text{K}_2\text{PtCl}_6, \ 4\text{Ag}, \ 4\text{AgCl}, \ \text{Pt}, \ 2\text{Ag}, \ 2\text{AgCl}. \]

It will be immediately obvious that such complete analyses, if concordant, afford valuable information regarding the purity of the potassium chlor-platinate. Nine values for the atomic weight of platinum may be deduced from each experiment by calculation from the following ratios:

(1) \( \text{Pt} : \text{K}_2\text{PtCl}_6 \)  
(2) \( \text{Pt} : 4\text{AgCl} \)  
(3) \( \text{Pt} : 2\text{AgCl} \)  
(4) \( \text{K}_2\text{PtCl}_6 : 4\text{AgCl} \)  
(5) \( \text{K}_2\text{PtCl}_6 : 2\text{AgCl} \)  
(6) \( \text{Pt} : 4\text{Ag} \)  
(7) \( \text{Pt} : 2\text{Ag} \)  
(8) \( \text{K}_2\text{PtCl}_6 : 4\text{Ag} \)  
(9) \( \text{K}_2\text{PtCl}_6 : 2\text{Ag} \)

The nine values for the atomic weight should, of course, be highly concordant if the pure dry salt has been accurately analysed. In the event of the original salt not being perfectly dry, all the ratios not involving the weight of the salt should yield the same figure for the atomic weight in question, but the other ratios should give slightly different results.

The analyses of potassium brom-platinate were effected in a manner strictly analogous to those of the chlor-platinate. The analyses of the ammonium salts were simpler; the initial reaction being as follows:

\[ (\text{NH}_4)\text{PtCl}_6 + 2\text{H}_2 = \text{Pt} + 2\text{NH}_4\text{X} + 4\text{HX}, \]

and the ammonium halide being volatile at the temperature employed, the halogen in the original salt was collected and determined in one operation instead of two.

Archibald’s results are as follows:

**Potassium Chlorplatinate**

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 13 expts.</td>
<td>( \text{K}_2\text{Cl}_6 : \text{Pt} ) : 100-000 : 67-097</td>
<td>whence ( \text{Pt} = 195-213 )</td>
</tr>
<tr>
<td>(2) 13 expts.</td>
<td>( 4\text{AgCl} : \text{Pt} ) : 100 000 : 34-049</td>
<td>( \text{Pt} = 195-219 )</td>
</tr>
<tr>
<td>(3) 14 expts.</td>
<td>( 2\text{AgCl} : \text{Pt} ) : 100-000 : 68-104</td>
<td>( \text{Pt} = 195-236 )</td>
</tr>
<tr>
<td>(4) 13 expts.</td>
<td>( 4\text{AgCl} : \text{K}_2\text{PtCl}_6 ) : 100-000 : 84-795</td>
<td>( \text{Pt} = 195-228 )</td>
</tr>
<tr>
<td>(5) 14 expts.</td>
<td>( 2\text{AgCl} : \text{K}_2\text{PtCl}_6 ) : 100-000 : 169-606</td>
<td>( \text{Pt} = 195-274 )</td>
</tr>
<tr>
<td>(6) 13 expts.</td>
<td>( 4\text{Ag} : \text{Pt} ) : 100-000 : 45-240</td>
<td>( \text{Pt} = 195-220 )</td>
</tr>
<tr>
<td>(7) 14 expts.</td>
<td>( 2\text{Ag} : \text{Pt} ) : 100-000 : 90-486</td>
<td>( \text{Pt} = 195-233 )</td>
</tr>
<tr>
<td>(8) 13 expts.</td>
<td>( 4\text{Ag} : \text{K}_2\text{PtCl}_6 ) : 100-000 : 112-66</td>
<td>( \text{Pt} = 195-208 )</td>
</tr>
<tr>
<td>(9) 14 expts.</td>
<td>( 2\text{Ag} : \text{K}_2\text{PtCl}_6 ) : 100-000 : 225-34</td>
<td>( \text{Pt} = 195-252 )</td>
</tr>
</tbody>
</table>

**Potassium Bromplatinate**

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10) 6 expts.</td>
<td>( \text{K}_2\text{Br}_2 : \text{Pt} ) : 100-000 : 35-005</td>
<td>whence ( \text{Pt} = 195-221 )</td>
</tr>
<tr>
<td>(11) 6 expts.</td>
<td>( 4\text{AgBr} : \text{Pt} ) : 100-000 : 25-989</td>
<td>( \text{Pt} = 195-225 )</td>
</tr>
<tr>
<td>(12) 6 expts.</td>
<td>( 2\text{AgBr} : \text{Pt} ) : 100-000 : 51-977</td>
<td>( \text{Pt} = 195-222 )</td>
</tr>
<tr>
<td>(13) 6 expts.</td>
<td>( 4\text{AgBr} : \text{K}_2\text{PtBr}_6 ) : 100-000 : 100-233</td>
<td>( \text{Pt} = 195-228 )</td>
</tr>
<tr>
<td>(14) 6 expts.</td>
<td>( 2\text{AgBr} : \text{K}_2\text{PtBr}_6 ) : 100-000 : 200-466</td>
<td>( \text{Pt} = 195-228 )</td>
</tr>
<tr>
<td>(15) 6 expts.</td>
<td>( 4\text{Ag} : \text{Pt} ) : 100-000 : 45-240</td>
<td>( \text{Pt} = 195-220 )</td>
</tr>
<tr>
<td>(16) 6 expts.</td>
<td>( 2\text{Ag} : \text{Pt} ) : 100-000 : 90-482</td>
<td>( \text{Pt} = 195-224 )</td>
</tr>
<tr>
<td>(17) 6 expts.</td>
<td>( 4\text{Ag} : \text{K}_2\text{PtBr}_6 ) : 100-000 : 174-48</td>
<td>( \text{Pt} = 195-220 )</td>
</tr>
<tr>
<td>(18) 6 expts.</td>
<td>( 2\text{Ag} : \text{K}_2\text{PtBr}_6 ) : 100-000 : 348-97</td>
<td>( \text{Pt} = 195-242 )</td>
</tr>
</tbody>
</table>

**Ammonium Chlorplatinate**

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(19) 5 expts.</td>
<td>( (\text{NH}_4)_2\text{PtCl}_6 : \text{Pt} ) : 100-000 : 78-447</td>
<td>whence ( \text{Pt} = 195-191 )</td>
</tr>
<tr>
<td>(20) 5 expts.</td>
<td>( 6\text{AgCl} : \text{Pt} ) : 100-000 : 22-689</td>
<td>( \text{Pt} = 195-216 )</td>
</tr>
<tr>
<td>(21) 5 expts.</td>
<td>( 6\text{AgCl} : (\text{NH}_4)_2\text{PtCl}_6 ) : 100-000 : 51-634</td>
<td>( \text{Pt} = 195-245 )</td>
</tr>
<tr>
<td>(22) 5 expts.</td>
<td>( 6\text{Ag} : \text{Pt} ) : 100-000 : 30-159</td>
<td>( \text{Pt} = 195-213 )</td>
</tr>
<tr>
<td>(23) 5 expts.</td>
<td>( 6\text{Ag} : (\text{NH}_4)_2\text{PtCl}_6 ) : 100-000 : 68-604</td>
<td>( \text{Pt} = 195-241 )</td>
</tr>
</tbody>
</table>
The results of Archibald thus furnish data for twenty-eight ratios, from which twenty-eight values for the atomic weight of platinum may be deduced. The extreme difference between these values is only 0.088 on a high atomic weight, a very satisfactory result. It will be noticed that the twenty-eight ratios experimentally established are theoretically not all different. Thus, (6) should equal (15), (7) should equal (16), and (22) should equal (27); and it is seen at a glance that these equalities hold experimentally within the very small limit of experimental error. Further, ratios (2), (8), and (20) yield the following closely agreeing values for the ratio Pt/AgCl, namely, 1.36196, 1.36208, and 1.36194; ratios (11), (12), and (25) yield the following concordant values for the ratio Pt/AgBr, namely, 1.08956, 1.08954, and 1.08950; and ratios (6), (7), (15), (16), (22), and (27) exhibit remarkable agreement in their values for the ratio Pt/Ag, namely, 1.80960, 1.80972, 1.80960, 1.80964, 1.80954, and 1.80960. It is therefore justifiable to assume that the mean value for the atomic weight of platinum deduced from Archibald's results represents a very close approximation to the true value. The arithmetic mean of the twenty-eight results is Pt = 195.227, the weighted mean, each result being weighted in proportion to the number of experiments made in fixing the ratio, is Pt = 195.229. Eliminating all ratios involving the weights of the chlor-platinates, since the salts may possibly have contained traces of water, the arithmetic mean of the values derived from the other ratios is Pt = 195.221, and the weighted mean is Pt = 195.224. Thus the atomic weight of platinum is most probably Pt = 195.22 with an uncertainty of two or three units in the second decimal place, the uncertainty being partly due to the small errors of experiment, and partly to possible slight errors in the other atomic weights used in the calculations.

In 1912 Schultz published five analyses of ammonium chlor-platinate, giving as a mean result Pt = 194.5. These experiments are clearly of little value.

The International Committee's table for 1918 gives

Pt = 195.2.

Uses.—Platinum is used in four different fields, namely, for chemical, electrical, and dental purposes, and for jewellery. For chemical purposes platinum is required both as metal and in the form of salts. The metal is used in the manufacture of crucibles, pyrometers, and for such apparatus as is required to withstand corrosive chemicals or high temperatures. Its salts are used in chemical analysis.

Platinum salts are useful in the production of certain photographic papers, which are of special value inasmuch as the photographic impression yielded by them is of superior quality and permanence.

Considerable quantities of platinum are used in preparing the

1 Schultz, Inaugural Dissertation, Erlangen, 1912.
catalyst required for contact-process sulphuric acid works. In 1915 about 44,000 oz. of the metal were used for this purpose, the loss per ton of acid ranging from a minute amount up to 0.25 gram.¹

Considerable quantities of platinum are required for electrical purposes. For example, electric furnaces use fairly large amounts of platinum; and the metal is also employed in the form of contact points.

It is estimated that about one-third of the total consumption of platinum is in dentistry, for which purpose it is used as pins in teeth, as foil, plate, and filling. Jewellery also absorbs an equal amount of platinum.

The World's Production of New Platinum in Troy Ounces ²

<table>
<thead>
<tr>
<th>Country</th>
<th>1913</th>
<th>1914</th>
<th>1915</th>
<th>1916</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russia (crude)</td>
<td>250,000</td>
<td>241,200</td>
<td>124,000</td>
<td>68,900</td>
</tr>
<tr>
<td>Canada (crude)</td>
<td>50</td>
<td>30</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>N.S. Wales and Tasmania (crude)</td>
<td>1,275</td>
<td>1,248³</td>
<td>303</td>
<td>222</td>
</tr>
<tr>
<td>Colombia (crude)</td>
<td>15,000³</td>
<td>17,500³</td>
<td>18,000</td>
<td>25,000</td>
</tr>
<tr>
<td>U.S.A. (domestic, crude)</td>
<td>483</td>
<td>570</td>
<td>742</td>
<td>750</td>
</tr>
<tr>
<td>U.S.A. (refined from foreign domestic matte and bullion)</td>
<td>1,100³</td>
<td>2,905</td>
<td>5,753</td>
<td>2,556</td>
</tr>
<tr>
<td>Borneo, Sumatra, etc.</td>
<td>200</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

Platinum Substitutes.—In consequence of the high price and scarcity of platinum numerous attempts have been made to supply cheaper substitutes.

Such substances must conform to certain specifications to be of any value, chief among which are:

(1) High melting-point. This is particularly important for many chemical and electrical purposes.

(2) Incorrodibility. Alkalies and acids should have a negligible effect at all temperatures, and oxidation of the substitute should not take place even on melting in air.

(3) Malleability, ductility, and high tensile strength are essential.

Alloys of palladium and gold have recently been recommended as platinum substitutes under the names of *rhotanium* (see p. 192) and *palan*.

As a substitute for platinum wire in the usual flame tests in qualitative analysis Kopa ⁵ recommends the employment of small quartz rods, 2–8 mm. in diameter, as they do not melt, and only impart a very faint colour to the flame. Asbestos threads dipped in a solution of orthophosphoric acid (1 part acid, 2 parts water) and heated to redness in a flame have also been recommended for a similar purpose.⁶

---

² Ibid., p. 592.
³ Estimated.
⁴ Mainly osmiridium.
⁵ Kopa, *Chem. Zeit.*, 1913, 37, 754.
⁶ Kirby, *Chem. News*, 1910, rox, 170,
As a substitute for platinum triangles, nichrome, an alloy of nickel and chromium (see p. 106), is recommended, as this is very resistant to oxidation at high temperatures.1

Metallic lead is used for sealing vacuum-tight quartz glass apparatus, such as cathode-ray tubes and mercury lamps.2 The method is stated to yield highly satisfactory results, and is adopted by the Silica Syndicate in the preparation of scientific apparatus.

ALLOYS

Aluminium.—Platinum readily alloys with aluminium, and a definite compound, PtAl2, containing 70·4 per cent. of platinum is formed. It is violet-black in colour, and yields dendritic and octahedral crystals. It occurs in increasing quantities in the alloys containing from 10 to 70 per cent. of platinum, and may be isolated from them by treatment with 5 per cent. hydrochloric acid, in which the compound is insoluble. Alloys containing less than 10 per cent. of platinum are white, malleable, and soft, consisting of aluminium and eutectic containing 9 per cent. of platinum. Alloys containing from 10 to 70 per cent. of platinum are also white, but hard and brittle; those with a platinum content of 70 to 90 per cent. are yellow and brittle, becoming white and malleable as the platinum increased beyond 90 per cent.3

Cadmium.—By heating platinum in hydrogen laden with cadmium vapour obtained from boiling metal, a white, crystalline, and very brittle compound, of formula PtCd2, is obtained.4

Copper.—With copper, platinum yields a series of very tenacious alloys. Those containing over 40 per cent. of platinum are white. The freezing-point curve of the alloys, containing from 30 to 100 per cent. of copper, falls continuously to the melting-point of copper. The metals yield a continuous series of mixed crystals.5

Gold.—Platinum and gold form a continuous series of mixed crystals, at any rate up to 60 per cent. of the former metal. The alloys containing over 40 per cent. of platinum are white.6

Iridium is usually alloyed with platinum in order to increase its hardness, although it reduces its ductility. The presence of iridium in platinum crucibles renders them subject to proportionately greater losses on heating at temperatures above 900° C. Below this temperature, however, and up to a content of at least 8 per cent. of iridium the loss on heating is negligible.7

An alloy of platinum and iridium, containing 10 per cent. of the latter metal, is attacked by boiling concentrated sulphuric acid to the extent of 0·10 gram per sq. decm. per hour at 365° C. On boiling the resulting solution with ammonia the platinum is deposited as sponge, whilst the solution becomes green, changing to deep violet upon addition of nitric acid in consequence of the presence of iridium salts.8

3 Chouriguine, Compt. rend., 1912, 155, 156. See also Bruneck, Ber., 1901, 34, 2733; Campbell and Eugène, J. Amer. Chem. Soc., 1902, 24, 256.
5 Doerningkel, Zeitseh. anorg. Chem., 1907, 54, 333. See also Debray, Compt. rend., 1887, 104, 1470.
8 Delépine, Compt. rend., 1906, 142, 631.
PLATINUM AND ITS COMPOUNDS 281

This 10 per cent. alloy is recommended for the construction of apparatus used in the preparation of fluorine. The same alloy was employed in the manufacture of the prototype metres and the geodesic rules, which latter are four metres in length, for the Comité Internationale des Poids et Mesures, and the Association Géodésique Internationale. The density of this alloy is high, namely, about 21·52 at 20° C., which renders it useful for standard weights, particularly in view of its incorrodibility and power of taking a high polish.

For the manufacture of standard rules, Matthey recommends an alloy containing not less than 85 per cent. of platinum and some 15 per cent. of iridium. For standard weights the same investigator suggests 20 per cent. of iridium, the remainder being platinum. This latter alloy is, like the previous one, both malleable and ductile, and has a density of 21·61. Alloys containing 25 per cent. of iridium are more difficult to work into sheet and wire, whilst alloys with 80 per cent. and 40 per cent. iridium can only be worked at a temperature just below the melting-point. When cold the last-named alloys are brittle.

Alloys of platinum and iridium are sometimes used in dentistry.

Iron.—See Part II of this Volume.

Lead.—Platinum readily alloys with lead, yielding three compounds, namely, Pb₄Pt, PbPt, and one the composition of which has not been determined. The alloys gradually increase in hardness with rise of platinum content from 0 to 45 per cent. Those containing up to 30 per cent. of platinum are readily fractured, and the fresh surfaces oxidise readily in air. The fact that platinum so readily alloys with lead is made use of in assaying the metal, since its alloys can be cupelled.

Magnesium unites with platinum to yield a crystalline compound, PtMg₂.

Osmium yields alloys with platinum characterised by hardness and tensile strength. They are very resistant to acid attack, and offer high electrical resistance. The alloys usually contain from 1 up to 10 per cent. of osmium.

Potassium unites with platinum on warming, yielding a hard but brilliant alloy, which is attacked by water.

Silver.—Alloys of platinum and silver have received a considerable amount of attention owing to their importance in assaying. No definite compound of the two metals appears to be formed.

Pure platinum is only very slowly attacked by boiling with concentrated sulphuric acid, and when its alloy with silver is submitted to similar treatment, the silver is more or less completely dissolved out, leaving the platinum as a black residue. Complete removal of the silver, however, is only effected when the initial proportion of that

1 See this Series, Vol. VIII.
3 Presumably at room temperature (15° to 20° C.). No temperature is mentioned by Matthey.
5 For earlier work on the alloys of platinum and lead see Bauer, Ber., 1870, 3, 836; 1871, 4, 440; Deville and Debray, Ann. Chim. Phys., 1859, [iii], 56, 385; Compt. rend., 1880, 90, 1195; Deville, ibid., 1887, 64, 1998.
8 V. Meyer, Ber., 1880, 13, 392.
metal in the alloy is some 90 per cent. or more. With smaller quantities of silver some is left behind in the platinum residue. This is well illustrated by the following data obtained by Thompson and Miller:

<table>
<thead>
<tr>
<th>Percentage Composition of Alloy.</th>
<th>Silver in residue (per cent.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum.</td>
<td>Silver.</td>
</tr>
<tr>
<td>10.39</td>
<td>89.61</td>
</tr>
<tr>
<td>20.59</td>
<td>79.41</td>
</tr>
<tr>
<td>31.46</td>
<td>68.54</td>
</tr>
<tr>
<td>37.89</td>
<td>62.11</td>
</tr>
<tr>
<td>57.05</td>
<td>42.95</td>
</tr>
</tbody>
</table>

A portion of the platinum tends to pass into solution with the silver, but by slightly diluting the sulphuric acid this may be prevented. According to Steinmann the most satisfactory results are obtained with a dilution of 100 volumes of acid to 22 volumes of water, the alloy being heated in this mixture, twice repeated, at about 240° C.

Although platinum is not attacked by nitric acid, yet it dissolves slightly when its alloys with silver are so treated, yielding a colloidal solution which is dark brown in colour. This is particularly the case with alloys containing about 20 per cent. of platinum. On standing for several days the platinum flocculates, and deposits as a black powder in a high state of subdivision, the solution becoming decolorised.

According to Spiller, nitric acid of density 1.42 will dissolve 0.75 to 1.25 per cent. of platinum from its alloy with 12 times its weight of silver, whilst a more concentrated acid leads to the separation of platinum black. A less concentrated acid dissolves less platinum.

The following data, taken from the results of Thompson and Miller, are interesting in that they show how imperfect is the separation of platinum from silver when alloys of the two metals are attacked by nitric acid of density 1.10:

<table>
<thead>
<tr>
<th>Composition of Alloy. Percentage.</th>
<th>Composition of Residue from 100 parts of Alloy.</th>
<th>Dissolved Platinum from 100 parts of Alloy.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.39</td>
<td>89.61</td>
<td>3.59</td>
</tr>
<tr>
<td>20.59</td>
<td>79.41</td>
<td>6.77</td>
</tr>
<tr>
<td>31.46</td>
<td>68.54</td>
<td>24.50</td>
</tr>
<tr>
<td>37.89</td>
<td>62.11</td>
<td>35.49</td>
</tr>
<tr>
<td>57.05</td>
<td>42.95</td>
<td>52.97</td>
</tr>
</tbody>
</table>

4 Thompson and Miller, *loc. cit.*
More recently somewhat similar results have been obtained by Koifman working with alloys containing from 0.219 to 5.162 per cent. of platinum.

Selenic acid dissolves out the silver from platinum alloys, leaving a residue of undissolved platinum.²

Alloys of silver and platinum are used by jewellers and by English dentists under the name of dental alloy, in the form of wire and sheet. Two qualities of these are recognised, the compositions of which vary somewhat with the makers, but approximate to the following:

<table>
<thead>
<tr>
<th>Silver</th>
<th>Platinum</th>
</tr>
</thead>
<tbody>
<tr>
<td>First quality</td>
<td>66</td>
</tr>
<tr>
<td>Second quality</td>
<td>75</td>
</tr>
</tbody>
</table>

These alloys are more durable and more resistant to corrosion than silver.

Platinum occurs in the following alloys used in the preparation of dental amalgams ⁴:

<table>
<thead>
<tr>
<th>Name</th>
<th>Tin</th>
<th>Silver</th>
<th>Gold</th>
<th>Platinum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fletcher's perfected standard alloy</td>
<td>62.80</td>
<td>30.30</td>
<td>5.80</td>
<td>1.60</td>
</tr>
<tr>
<td>S. S. White's globe</td>
<td>53.36</td>
<td>44.74</td>
<td>1.50</td>
<td>0.40</td>
</tr>
<tr>
<td>Welch's gold and platinum alloy:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Old</td>
<td>54.00</td>
<td>44.00</td>
<td>1.80</td>
<td>0.70</td>
</tr>
<tr>
<td>(2) New</td>
<td>51.90</td>
<td>46.00</td>
<td>1.70</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Sodium and platinum alloy when brought together at a high temperature or pressure.⁵

Thallium.—Platinum alloys with thallium, yielding a compound, PtTl, which resembles, at any rate in its physical properties, the compound PtPb. The alloy is conveniently formed by throwing platinum sponge upon the surface of fused thallium. The compound yields steel-grey, prismatic needles, and is extracted by treating an alloy containing less than 10 per cent. of platinum with dilute nitric acid. Its density is 15.65 at 14° C.; hardness 3; melting-point 685° C.; and specific heat 0.0450. When subjected to continued heating above its melting-point, a little thallium is lost, but pure platinum is not obtained even on prolonged fusion in the oxyhydrogen flame. When boiled with aqua regia, thallium chlor-platinate is obtained as an insoluble compound.

Insoluble in hydrochloric acid, the alloy is only superficially attacked by sulphuric or nitric acid, and by fusion with potassium hydrogen sulphate. It readily dissolves in molten zinc, lead, or silver, and amalgamates with mercury.⁶

Tin.—Platinum readily alloys with tin. The complicated freezing-point

¹ Koifman, Arch. Sci. phys. nat., 1915, [iv], 40, 509.
² Hradecky, Monatsh., 1915, 36, 289.
³ Including sometimes a little copper.
⁴ Taken from E. A. Smith, Dental Metallurgy (Churchill, 1910), p. 149.
⁵ V. Meyer, Ber., 1880, 13, 392. See also Haber and Sack, Zeitsch. Elektrochem., 1902, 8, 245; Sack, Zeitsch. anorg. Chem., 1903, 34, 286.
⁶ Hacksplll, Compt. rend., 1908, 146, 820.
curve for Pt—Sn is indicative of the formation of several compounds,\textsuperscript{1} namely, Pt\textsubscript{3}Sn, which is only stable below 1870° C. and decomposes above that temperature into crystals of platinum and a fused mixture containing 80 per cent. of platinum; PtSn; Pt\textsubscript{3}Sn\textsubscript{4}, and possibly a polymorphous form of this alloy; and a fourth compound PtSn\textsubscript{4} (Podkopeeff) or Pt\textsubscript{3}Sn\textsubscript{3} (Doerinckel).

The alloys containing up to 30 per cent. of platinum are scarcely any harder than their constituents; above 30 per cent. the hardness rapidly increases with the platinum, reaching a maximum with 80 per cent. of that metal.

The tetrastannide, PtSn\textsubscript{4}, was first isolated by Deville and Debray \textsuperscript{2} by treating an alloy containing 2 per cent. of platinum with dilute hydrochloric acid. It remained behind as brilliant, insoluble lamellæ.

The sesquistannide, Pt\textsubscript{2}Sn\textsubscript{3}, was described by Schützenberger \textsuperscript{3} in 1884. The existence of a compound of formula Pt\textsubscript{4}Sn\textsubscript{3} has also been assumed,\textsuperscript{4} but this is not supported by an examination of the freezing-point curve.

**Zinc.**—When platinum is heated in hydrogen laden with zinc vapour from the boiling metal, the compound PtZn\textsubscript{2} is formed. Another compound, PtZn, has also been obtained.\textsuperscript{5}

**Platinum Amalgam** is obtained by trituration of platinum sponge with mercury in a warm mortar; it cannot be obtained by direct union of platinum foil and mercury.

The amalgam has a silvery appearance, and with 12 per cent. of platinum is soft and greasy to the touch, but higher percentages of platinum increase its stiffness. When heated strongly the mercury is volatilised and platinum remains as a grey residue.

When shaken with water for some fifteen seconds, platinum amalgam is converted into an emulsion of butter-like consistency, and having a volume some five times that of the original amalgam. It is quite stable between 100° C. and — 80° C. in air, but in vacuo it diminishes somewhat in volume, a little water and gas being liberated. When cooled to — 80° C. its appearance under the microscope is cellular, water being disseminated throughout the interstices of the amalgam.

Platinum amalgam emulsifies in a similar manner when shaken with dilute sulphuric acid; with aqueous ammonia, ammonium chloride, or sodium chloride; and in contact with several organic solvents, such as alcohol, acetone, etc.\textsuperscript{6}

Microscopic examination proves that an amalgam is formed during the simultaneous reduction of platinum and mercury from aqueous solutions of their salts.\textsuperscript{7}

**PLATINUM AND FLUORINE**

Platinum unites with fluorine when heated with it, but attempts to prepare fluorides of platinum without employing elementary fluorine

---


\textsuperscript{2} Deville and Debray, \textit{Compt. rend.}, 1887, 104, 1470, 1577.

\textsuperscript{3} Schützenberger, \textit{ibid.}, 1884, 83, 985.

\textsuperscript{4} Levy and Bourgeois, \textit{ibid.}, 1882, 94, 1365.

\textsuperscript{5} Hodgkinson, Waring, and Desborough, \textit{Chem. News}, 1899, 80, 185.

\textsuperscript{6} Moissan, \textit{Compt. rend.}, 1907, 144, 593 ; Lebeau, \textit{ibid.}, p. 843.

\textsuperscript{7} Tarugi, \textit{Gazzetta}, 1903, 33, ii, 171.
have hitherto proved abortive. For example, fusion of the metal with potassium hydrogen fluoride, or heating of the chloride in an atmosphere of anhydrous hydrogen fluoride, leads to no result. A substance consisting very probably of:

**Platinum Difluoride, Platinous Fluoride**, PtF₂, was obtained by Moissan together with the tetrafluoride by heating platinum wire to 500° or 600° C. in a current of fluorine. The tetrafluoride is soluble in water, but the difluoride remains attached to the surface of the metal as a yellowish green layer, insoluble in water. Upon ignition it decomposes into fluorine and platinum.

**Platinum Tetrafluoride, Platinic Fluoride**, PtF₄, obtained by passage of fluorine over platinum wire heated to 500° or 600° C., contained in a thick platinum or fluor spar tube, is deep red when fused, but yields yellow crystals. These are very hygroscopic, and dissolve in water with considerable heat evolution.

The aqueous solution of this salt is fawn-coloured and unstable, readily decomposing into hydrofluoric acid and a hydrated oxide of platinum.

At red heat platinic fluoride dissociates, evolving fluorine, a residue of crystalline platinum remaining.

**PLATINUM AND CHLORINE**

Evidence has been obtained of the existence of **Platinum Monochloride**, PtCl, which is stable as a yellowish green substance between 581° and 583° C.

**Platinum Dichloride**, PtCl₂.—This salt, also known as **Platinous Chloride**, may be prepared by evaporating a solution of the tetrachloride to dryness and heating the residue to about 300° or 350° C. under constant stirring. Any unchanged platinic acid is removed by washing with water.

Platinum dichloride also results, mixed with a little tetrachloride, when platinum sponge or, better, platinum black, obtained by reduction of ammonium chlor-platinate by hydrogen gas at 100° C., is heated in chlorine to 360° C. It is obtained in a more pure condition by heating chlor-platinic acid, H₂PtCl₄, or the hydrated acid chloride, namely, trichlor-platinic acid, PtCl₃·HCl·2H₂O or H₃PtCl₄(OH)H₂O, to 100° C.

Platinum dichloride is a greenish grey or brown powder, its colour varying according to the method of preparation. Insoluble in water, it dissolves in hydrochloric acid to yield a solution of chlor-platinous acid, H₂PtCl₃, and in aqua regia to chlor-platinic acid, H₃PtCl₄. Caustic alkalies decompose it, yielding a black deposit of hydrated platinous oxide. With ammonia, complex ammino derivatives are formed.

**Tetrachlor-platinous Acid**, H₂PtCl₄, has not been isolated in a pure state, but exists in solution when platinous chloride is dissolved in hydrochloric acid, and when chlor-platinic acid is reduced by sulphur dioxide, the yellow solution becoming red in colour.

1 Ruff and his co-workers, *Ber.*, 1913, 46, 920.
3 Moissan, *Compt. rend.*, 1889, 109, 807.
4 L. Wöhler and Streicher, *Ber.*, 1913, 46, 1591.
5 Berzelius, *Schweigger’s J.*, 1813, 7, 55.
8 See this Series, Vol. X.
In dilute solution the pure acid results on decomposing the barium or silver salt with the requisite amount of sulphuric or hydrochloric acid. The solution cannot be concentrated, however, without decomposition, hydrogen chloride being evolved. When evaporated in vacuo, a residue of hydrated acid dichloride or trichlor-hydroxy-platinous acid is left, namely, $\text{PtCl}_2 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ or $\text{H}_2\text{PtCl}_3(\text{OH}) \cdot \text{H}_2\text{O}$. If the evaporation is continued at 100° C. platinous chloride results.

**Tetrachlor-platinates, $\text{M}_2\text{PtCl}_4$**

Salts of tetrachlor-platinous acid are known as *tetrachlor-platinates*, and have the general formula $\text{M}_2\text{PtCl}_4$.

They are both stable and well known. They may be prepared in a variety of ways, chief amongst which are:

1. Addition of chlor-platinous acid or a solution of platinous chloride to a metallic carbonate or chloride. For this purpose the chlor-platinous acid is best made by dissolving platinous chloride in hydrochloric acid. This ensures the freedom of the final product from the metallic chlor-platinate. A less troublesome method is to reduce chlor-platinic acid with sulphur dioxide if a pure product is not required, but this is not easy to carry out satisfactorily otherwise. If, for example, reduction of the chlor-platinic acid is not complete, the metallic platinite will be contaminated with platinate. If, on the other hand, excess of sulphur dioxide is present, the metallic chlor-platinite becomes contaminated with sulphite derivatives.

2. Probably the most convenient method of preparing metallic chlor-platinites consists in reducing the corresponding chlor-platinates. This may be effected with potassium oxalate in concentrated aqueous solution at the boiling-point, and containing a trace of iridium, the reaction proceeding according to the equation:

$$\text{M}_2\text{PtCl}_4 + \text{K}_2\text{C}_2\text{O}_4 = \text{M}_2\text{PtCl}_4 + 2\text{KCl} + 2\text{CO}_2.$$ 

Hydrogen sulphide, cuprous chloride, and the last named along with powdered zinc, have been used as reducing agents, but are open to several objections.

3. Double decomposition of metallic sulphates and barium chlor-platinite. Thus:

$$\text{M}_2\text{SO}_4 + \text{BaPtCl}_4 = \text{BaSO}_4 + \text{M}_2\text{PtCl}_4.$$ 

The clear solution containing the soluble chlor-platinite is decanted or filtered free from the insoluble barium sulphate, and concentrated.

The chlor-platinites are mostly soluble salts yielding red solutions readily distinguished from solutions of the chlor-platinates, which are yellow. The silver, lead, mercury, and thallium salts are almost insoluble in water.

Chlor-platinites are oxidised by chlorine and by hypochlorites to chlor-platinates, whilst nascent hydrogen reduces them in aqueous solution with separation of metallic platinum.

When their solutions are warmed and a current of hydrogen sulphide

4 Thomsen, *ibid.*, 1877, [ii], 15, 295.
is passed through, platinous sulphide is obtained as a black precipitate; whilst sulphur dioxide under like conditions effects their decolorisation, platinosulphites being produced. With ammonia, ammino derivatives are obtained.

Ammonium Tetrachlor-platinite, \((\text{NH}_4)_2\text{PtCl}_4\), crystallises in long, red, orthorhombic prisms, which are soluble in water.

Potassium Tetrachlor-platinite, \(\text{K}_2\text{PtCl}_4\), is obtained technically \(^1\) by passing sulphur dioxide into a solution of chlor-platinic acid, maintained at about 100° C., until a sample yields no precipitate with ammonium chloride. This indicates that reduction is complete. A hot solution of twice the calculated quantity of potassium chloride is added, and the chlor-platinite allowed to crystallise out. It is washed with alcohol and dried in the absence of light.\(^2\)

Although a solution of pure potassium hexachlor-platinate, \(\text{K}_2\text{PtCl}_6\), is not reduced by boiling with potassium oxalate, reduction readily takes place if a trace of iridium in solution is added.\(^3\) In the presence of much iridium the reaction may even become violent. The density of potassium tetrachlor-platinite is 3.3056 at 20° C., and 3.2909 at 21° C.,\(^4\) whilst its heat of formation is\(^5\):

\[
[\text{Pt}] + 2(\text{Cl}_2) + 2\text{KCl} = [\text{K}_2\text{PtCl}_4] + 45.17 \text{ Cals.}
\]

The following tetrachlor-platinites have also been prepared:

- Barium,\(^6\) \(\text{BaPtCl}_4\cdot3\text{H}_2\text{O}\);
- Casium,\(^7,8\) \(\text{Cs}_2\text{PtCl}_4\);
- Calcium,\(^7\) \(\text{CaPtCl}_4\cdot8\text{H}_2\text{O}\);
- Cerium,\(^7\) \(2\text{CeCl}_3\cdot4\text{PtCl}_2\cdot21\text{H}_2\text{O}\);
- Cobalt,\(^7\) \(\text{CoPtCl}_4\cdot6\text{H}_2\text{O}\);
- Copper,\(^7\) \(\text{CuPtCl}_4\cdot6\text{H}_2\text{O}\);
- Glucinium,\(^7\) \(\text{GIPtCl}_4\cdot5\text{H}_2\text{O}\);
- Iron (ferrous),\(^7\) \(\text{FePtCl}_4\cdot7\text{H}_2\text{O}\);
- Lead,\(^6\) \(\text{PbPtCl}_4\);
- Lithium,\(^7\) \(\text{Li}_2\text{PtCl}_4\cdot4\text{H}_2\text{O}\);
- Magnesium,\(^7\) \(\text{MgPtCl}_4\cdot6\text{H}_2\text{O}\);
- Manganese,\(^7\) \(\text{MnPtCl}_4\cdot6\text{H}_2\text{O}\);
- Nickel,\(^7\) \(\text{NiPtCl}_4\cdot6\text{H}_2\text{O}\);
- Rubidium,\(^7,8\) \(\text{Rb}_2\text{PtCl}_4\);
- Sodium,\(^7\) \(\text{Na}_2\text{PtCl}_4\cdot4\text{H}_2\text{O}\);
- Strontium,\(^7\) \(\text{SrPtCl}_4\cdot6\text{H}_2\text{O}\);
- Thallium,\(^9\) \(\text{Tl}_2\text{PtCl}_4\);
- Zinc,\(^7\) \(\text{ZnPtCl}_4\cdot6\text{H}_2\text{O}\);
- Zirconyl,\(^7\) \((\text{ZrO})\text{PtCl}_4\).

Trichlor-hydroxy-platinous Acid, \(\text{H}_2\text{PtCl}_3(\text{OH})\).—The hydrate of this acid, namely, \(\text{H}_2\text{PtCl}_3(\text{OH})\cdot\text{H}_2\text{O}\), is obtained as a reddish brown

---

\(^1\) For other methods see Carey Lea, Amer. J. Sci., 1894, [iii], 48, 397; Thomsen, J. prakt. Chem., 1877, [ii], 15, 295; Magnus, Pogg. Annalen, 1828, 14, 239.

\(^2\) Klason, Ber., 1904, 37, 1360.


\(^4\) Clarke, Amer. J. Sci., 1878, [iii], 16, 206.

\(^5\) Thomsen, loc. cit., p. 436.

\(^6\) Lang, J. prakt. Chem., 1862, 86, 126.


\(^8\) Böttger, J. prakt. Chem., 1864, 6, 91, 251.

deliquescent mass on evaporating an aqueous solution of tetrachlor-platinous acid \textit{in vacuo} over sulphuric acid and potash.\textsuperscript{1,2}

It dissolves in water, yielding a reddish brown solution with an acid reaction. Heated to 100° C. it loses water and hydrogen chloride, yielding a residue of platinum dichloride.

**Silver Trichlor-hydroxy-platinite**, \(\text{Ag}_2\text{PtCl}_3(\text{OH})\), is obtained \textsuperscript{2} as a brown precipitate on adding a saturated solution of silver acetate to one of trichlor-hydroxy-platinous acid in the cold.

**Lead Trichlor-hydroxy-platinite**, \(\text{PbPtCl}_3(\text{OH})\), is obtained \textsuperscript{2} in a similar manner to the preceding salt. It is somewhat darker in colour.

**Dichlor-di-hydroxy-platinous Acid**, \(\text{H}_2\text{PtCl}_3(\text{OH})_2\). — Evidence that this acid can exist is not altogether wanting.\textsuperscript{2} A silver salt, having a composition closely corresponding to the formula \(\text{Ag}_2\text{PtCl}_3(\text{OH})_2\) has been obtained.\textsuperscript{2}

**Platinum Trichloride**, \(\text{PtCl}_3\), results \textsuperscript{3} when platinum tetrachloride is heated to 890° C. in a current of pure, dry chlorine for several hours.

It is a greenish black powder, slightly soluble in cold water, but rapidly dissolved by the boiling liquid, yielding a reddish brown acid solution which is possibly \textit{trichlor-di-hydroxy-platinous acid}, \(\text{H}_2\text{PtCl}_3(\text{OH})_2\), analogous to the tetrachlor-di-hydroxy-platinic acid, \(\text{H}_3\text{PtCl}_4(\text{OH})_2\), obtained when the tetrachloride is dissolved in water (see p. 289). Prolonged boiling with water causes partial hydrolysis, an oxychloride and free hydrochloric acid resulting.

The trichloride is almost insoluble in concentrated hydrochloric acid at room temperature, but on warming the two, decomposition takes place, the di- and tetra-chlorides of platinum resulting.

**Pentachlor-platinous Acid** has not as yet been isolated in a free state although its presence has been detected in solution \textsuperscript{4} when chlorine is passed into a solution of tetrachlor-platinous acid, since it yields with caesium chloride the characteristic green precipitate of caesium pentachlor-platinite, \(\text{Cs}_2\text{PtCl}_5\), which is the only salt of this acid at present known.

**Caesium Pentachlor-platinite**, \(\text{Cs}_2\text{PtCl}_5\), is obtained \textsuperscript{4} when chlorine is passed into a cold solution of caesium tetrachlor-platinite, \(\text{Cs}_2\text{PtCl}_4\); it also results when hydrated platinum sesquioxide is dissolved in hydrochloric acid containing caesium chloride. It is a green, crystalline, insoluble salt. When warmed with water it readily decomposes, yielding the tetrachlor-platinite. Exposure to sunlight likewise accelerates its decomposition.

**Platinum Tetrachloride, Platinic Chloride**, \(\text{PtCl}_4\).—This salt was first prepared in a hydrated form by Norton,\textsuperscript{5} who, however, failed to isolate the anhydrous salt. This latter may be obtained by heating partially dehydrated chlor-platinic acid in a current of chlorine at 360° C.\textsuperscript{6} The possibility of preparing it in this way has been disputed,\textsuperscript{7} but Guttier, who carried out a number of experiments with chlor-platinic acid under a variety of conditions, was able to prepare the salt quite easily. In the neighbourhood of 60° C. the crystals melt in their

---

\textsuperscript{1} Nilson, \textit{J. prakt. Chem.}, 1877, [ii], 15, 260.
\textsuperscript{2} Miolati and Pendini, \textit{Zeitsch. anorg. Chem.}, 1903, 33, 264.
\textsuperscript{3} L. Wöhler and Martin, \textit{Ber.}, 1909, 42, 3958.
\textsuperscript{4} L. Wöhler and Martin, \textit{loc. cit.}, p. 4100.
\textsuperscript{5} Norton, \textit{J. prakt. Chem.}, 1870, 2, 469.
\textsuperscript{7} Rosenheim and Loewenstamm, \textit{Zeitsch. anorg. Chem.}, 1903, 37, 394.
combined water; a little later the water boils off and the mixture thickens. The final stages of the reaction are carried out with a slow rise of temperature.

One method consisted in suspending ammonium chlor-platinic acid in a small quantity of water, and decomposing it by the passage of chlorine gas. In order to avoid the formation of explosive nitrogen chloride the reaction should be carried out at 100° C.¹ The product, namely, chlor-platinic acid in solution, is evaporated to dryness in vacuo, and heated in dry chlorine at 350° to 360° C., care being taken not to exceed this latter temperature. The mass foams somewhat, on account of the liberation of water and hydrogen chloride, and is gradually converted into the tetrachloride.²

Gutbier, however, recommends heating chlor-platinic acid in a current of dry chlorine to a temperature not exceeding 360° C. in an apparatus containing diphenylamine.

Platinum tetrachloride is also obtained by heating chlor-platinic acid to 165° C. in a current of hydrogen chloride for fifteen hours.³

Platinum tetrachloride is not formed by merely heating chlor-platinic acid in air, because it decomposes before the whole of the hydrogen chloride is eliminated, yielding the dichloride.⁴ When heated to 370° C. in an atmosphere of chlorine it begins to dissociate⁵:

\[ \text{PtCl}_4 \rightleftharpoons \text{PtCl}_2 + \text{Cl}_2. \]

Platinum tetrachloride is reddish brown in colour, somewhat hygroscopic, and moderately soluble in warm water with evolution of heat (see below). It is but slightly soluble in alcohol, but easily soluble in acetone.⁶

When exposed to the air, water is absorbed and the salt assumes a bright yellow colour, yielding a compound of composition represented by the formula \( \text{H}_2\text{PtCl}_4\cdot \text{O}_2\text{H}_2\text{O} \). Its aqueous solution is stable, admitting even of distillation without decomposition, and has an acid reaction, decomposing carbonates with evolution of carbon dioxide. It is usually regarded as containing tetrachlor-di-hydroxy-platinic acid,⁷ \( \text{H}_2\text{PtCl}_4(\text{OH})_2 \) or \( \text{PtCl}_4\cdot 2\text{H}_2\text{O} \), and this receives support from the fact that upon electrolysis of the solution it is found that platinum is contained in the complex anion.⁸

Platinum tetrachloride is reduced in solution by iodine at the ordinary temperature to the dichloride:

\[ \text{PtCl}_4 + \text{I}_2 = \text{PtCl}_2 + 2\text{ICl}. \]

This reaction is made the basis of a volumetric method for estimating platinum (see p. 341).

¹ Pigeon, loc. cit.
² Gutbier and Heinrich, Zeitsch. anorg. Chem., 1913, 81, 378.
⁵ L. Wöhler and Streicher, Ber., 1913, 46, 1591.
⁶ Rosenberg and Loewenstamm, loc. cit.
⁷ Kohlrausch, Wied. Annalen, 1897, 63, 423.
⁹ Grampe, Ber., 1874, 7, 1721.
The heat of formation 1 of platinum tetrachloride is:

\[ \text{[Pt]} + 2(\text{Cl}_2) = [\text{PtCl}_4] + 59.4 \text{ Cals.} \]

and its heat of solution in water is:

\[ [\text{PtCl}_4] + \text{Aq.} = \text{PtCl}_4 \cdot \text{Aq.} + 19.58 \text{ Cals.} \]

When dry, platinum tetrachloride is reduced to the metal by a current of hydrogen even below 80°C.2 Its solution is reduced by powdered cobalt, with precipitation of metallic platinum. Thus 1:

\[ \text{PtCl}_4 \cdot \text{Aq.} + 2(\text{Co}) = [\text{Pt}] + 2\text{CoCl}_2 \cdot \text{Aq.} + 109.98 \text{ Cals.} \]

**Hydrates of Platinum Tetrachloride.**—Platinum chloride combines with water to yield a series of hydrates. The *octahydrate*, PtCl₂.8H₂O, crystallises from aqueous solutions of the salt in the form of red needles.3 The *pentahydrate*, PtCl₂.5H₂O, was first obtained by Norton4 and studied by Jørgensen.5 It results on decomposing silver chlor-platinate with boiling water, filtering off the silver chloride and crystallising over sulphuric acid. It crystallises in apparently monoclinic prisms, red in colour. When dissolved in water and the solution evaporated, the octahydrate separates out. Heated to 100°C, the pentahydrate loses 4 molecules of water, being converted into the monohydrate (see below).

The *tetrahydrate*, PtCl₂.4H₂O, is the stable form at the ordinary temperature. It is obtained by allowing higher hydrates to effloresce in dry air,1 or by dissolving platinum hydroxide in a solution of chlor-platinate, and concentrating to crystallisation.6 The crystals are deliquescent, and, upon warming to 50°C in a current of dry hydrogen chloride, yield chlor-platinic acid.

The *dihydrate*, PtCl₂.2H₂O or H₂PtCl₄(OH)₂, has not been isolated in the pure state. It exists in solution when platinum tetrachloride is dissolved in water, and is described under the name of tetrachloro-dihydroxy-platinic acid (see p. 296).

The *monohydrate*, PtCl₂.H₂O, results when the pentahydrate 4 or the tetrahydrate 1 is heated to 100°C. When heated to 360°C it leaves a residue of dichloride.

**Hexachlor-platinic Acid**, H₂PtCl₆, is obtained in solution when platinum tetrachloride is dissolved in aqueous hydrochloric acid.

The usual method of preparing it consists in dissolving platinum in aqua regia.

The metal may, however, contain iridium which, although insoluble in aqua regia when by itself, yet dissolves when alloyed with platinum. The metal is therefore attacked by aqua regia on the water-bath, and the concentrated solution diluted, rendered alkaline with sodium carbonate, and reduced with formate. After warming, the precipitated metals are dried and ignited in a crucible whereby the iridium is rendered insoluble in aqua regia. Treatment with this latter reagent effects the solution of the platinum. To remove all nitrous compounds the solution is repeatedly evaporated and taken up again with concentrated

---

5 Jørgensen, *ibid.*, 1877, 16, 345.
6 Engel, *Bull. Soc. chim.*, 1888, [ii], 50, 100.
hydrochloric acid. Any chlor-platinous acid, H₂PtCl₆, is converted into chlor-platinic acid by saturating with chlorine in the warm.

Platinum scrap is conveniently worked up into chlor-platinic acid by alloying with zinc under a layer of borax. The melt is treated with hydrochloric acid, which removes most of the zinc, and the finely divided platinum is dissolved in aqua regia.

The solution thus obtained is contaminated with a little zinc. It is therefore treated either with a rod of pure zinc which precipitates the platinum, or with hydrogen sulphide whereby the sulphide is precipitated and ignited. In both cases the resulting metal is dissolved in aqua regia, repeatedly evaporated with hydrochloric acid, excess of acid being finally removed by evaporation and the residue taken up with water.¹

Platinum sponge is soluble in concentrated hydrochloric acid saturated with chlorine ²; platinum black, if it has not been ignited, dissolves in concentrated hydrochloric acid in the presence of hydrogen peroxide ³; whilst compact platinum passes into solution when treated with a mixture of chloric acid and concentrated hydrochloric acid.⁴

In each of these cases a solution of chlor-platinic acid is obtained entirely free from nitrogen compounds, and in a high state of purity if the original metal consisted of pure platinum.

The acid may also be obtained electrolytically ⁵ by passing an electric current through concentrated hydrochloric acid containing precipitated platinum in a fine state of subdivision, using platinum foil as electrodes. The anodic chlorine attacks the finely divided metal, yielding the tetra-chloride, which dissolves in the liquid to form the acid. The finely divided metal is conveniently prepared for this purpose by precipitation with metallic zinc from a solution of a platinum salt. On concentrating the solution to obtain the pure chlor-platinic acid it is advisable to introduce a small quantity of chlorine to ensure the absence of platinous compounds.

On concentrating the solution, chlor-platinic acid crystallises out in the form of reddish brown needles containing 6 molecules of water, thus: H₂PtCl₆.6H₂O.⁶ The crystals are deliquescent, soluble in water, alcohol, and ether; density ⁷ 2.481.

Equivalent solutions of chlor-platinic acid and its sodium salt exhibit the same absorption spectrum.⁸ It is reasonable, therefore, to assume that similar negative ions exist in both solutions. If the formula Na₂PtCl₆ be accepted for the sodium salt, that of the free acid is H₂PtCl₆, and not 2HCl·PtCl₄.

When heated, the crystals melt at 60° C. in their own combined water; if maintained at 100° C. in vacuo in the presence of potash, pentachlor-hydroxy-platinic acid, PtCl₄·HCl.2H₂O or H₂PtCl₆(OH).H₂O, is left as a residue in the form of reddish brown crystals.⁹ At higher temperatures platinum dichloride is formed. It does not, upon mere

⁷ Boedecker, Jahresber., 1860, p. 16.
⁸ Hantzsche, Ber., 1908, 41, 1216.
ignition in air, yield the anhydrous tetrachloride, PtCl₄, since this decomposes before the whole of the hydrogen chloride has been eliminated. Consequently, to prepare the tetrachloride it is necessary to heat chlor-platinic acid either in dry hydrochloric acid or in chlorine.

When a concentrated solution of chlor-platinic acid is poured into concentrated sulphuric acid, the tetrahydrate, H₂PtCl₆·4H₂O, is obtained as a yellow precipitate. The anhydrous acid has not been isolated.

Chlor-platinic acid decomposes metallic carbonates, and unites with bases to form salts known as chlor-platinates, M₂PtCl₆. Hydrogen sulphide reduces it to chlor-platinous acid, H₂PtCl₄, and after a time precipitates some of the platinum in the form of its black disulphide, PtS₂.

Sulphur dioxide likewise reduces the acid to chlor-platinous acid, and if added in excess gives rise to complex sulphite derivatives. Yellow phosphorus reduces it to the metal, whilst hydrogen phosphide causes hypophosphites or phosphides to form, according to circumstances.

The heats of formation of chlor-platinic acid are as follow ¹:

\[
\text{[PtCl}_4\text{]} + 2\text{HCl} \cdot \text{Aq.} = \text{H}_2\text{PtCl}_6 \cdot \text{Aq.} + 24.8 \text{ Cals.}
\]

and ²

\[
\text{[Pt]} + 2(\text{Cl}_2) + 2\text{HCl} \cdot \text{Aq.} = \text{H}_2\text{PtCl}_6 \cdot \text{Aq.} + 84.6 \text{ Cals.}
\]

The heat of solution of the hexahydrated crystals is ¹:

\[
\text{[H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O]} \cdot \text{Aq.} = \text{H}_2\text{PtCl}_6 \cdot \text{Aq.} + 4.34 \text{ Cals.}
\]

**Hexachlor-platinates**

Salts of hexachlor-platinic acid may be conveniently divided into three groups, namely:

1. Anhydrous salts of general formula M₂PtCl₆.
2. Hexahydrated salts, chiefly of the divalent metals, of general formula R₂PtCl₆·6H₂O.
3. Salts of divalent, trivalent, and tetravalent metals, containing varying quantities of water.

They may be obtained in several ways, namely:

1. By direct action of chlor-platinic acid upon the hydroxides or carbonates of metals. For example:

\[
2\text{KOH} + \text{H}_2\text{PtCl}_6 = \text{K}_2\text{PtCl}_6 + 2\text{H}_2\text{O}.
\]

2. By mixing solutions of soluble metallic chlorides and chlor-platinic acid. For example:

\[
2\text{NH}_4\text{Cl} + \text{H}_2\text{PtCl}_6 = (\text{NH}_4)_2\text{PtCl}_6 + 2\text{HCl}.
\]

This is a particularly useful method to adopt when a quantitative determination of platinum is required (see p. 341) since ammonium chlor-platinate is relatively insoluble in water, and still less soluble in alcohol.

3. A similar reaction to the preceding takes place when other salts than chlorides are added to chlor-platinic acid. For example, silver chloride is insoluble in water, but on adding the nitrate to a cold solution of the acid, silver chlor-platinate is immediately precipitated:

\[
2\text{AgNO}_3 + \text{H}_2\text{PtCl}_6 = \text{Ag}_2\text{PtCl}_6 + 2\text{HCl}.
\]

¹ Pigeon, loc. cit.
(4) By double decomposition of a soluble chlor-platinate, such as the sodium salt Na₂PtCl₆, with a salt of a metal yielding an insoluble chlor-platinate, such as, for example, silver.

The chlor-platinates are mostly of a yellow colour, the insoluble salts, namely, those of potassium, rubidium, caesium, ammonium, and silver, crystallising in the anhydrous condition in the form of cubic octahedra, isomorphous with the chlor-iridates and chlor-osmates. The more soluble chlor-platinates, namely, those of sodium, magnesium, zinc, etc., crystallise with 6 molecules of water, and are isomorphous with the chlor-stannates.

Both ammonium and potassium chlor-platinates, on account of their insolubility in alcohol, are used in the quantitative estimation of platinum. The former salt upon ignition yields a very pure platinum sponge. The solubilities of the more important chlor-platinates in water at 18° C. are given in the following table:

<table>
<thead>
<tr>
<th>Chlor-platinate</th>
<th>Grams of M₂PtCl₆ in 100 grams of Water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>Almost nil</td>
</tr>
<tr>
<td>Cæsium</td>
<td>0·08</td>
</tr>
<tr>
<td>Rubidium</td>
<td>0·14</td>
</tr>
<tr>
<td>Ammonium</td>
<td>0·67</td>
</tr>
<tr>
<td>Potassium</td>
<td>1·03</td>
</tr>
<tr>
<td>Sodium</td>
<td>c. 40</td>
</tr>
</tbody>
</table>

**Group I.—Anhydrous Salts of General Formula M₂PtCl₆**

**Ammonium Chlor-platinate** (NH₄)₂PtCl₆, is closely similar in appearance to the potassium salt, with which it is isomorphous. It crystallises in regular octahedra.

The solubility of ammonium chlor-platinate in water at various temperatures is as follows:

| Temperature °C | Grams (NH₄)₂PtCl₆ per 100 grams H₂O | 15·5 | 100 |

When heated, ammonium chlor-platinate decomposes in accordance with the equation:

\[ 3(NH₄)₂PtCl₆ = 3Pt + 16HCl + 2NH₄Cl + 2N₂ \]

the metal being left behind as a dull grey, soft and porous mass known as spongy platinum or platinum sponge.

The density of the salt is 3·084.

**Cæsium Chlor-platinate** Cs₂PtCl₆, yields yellow cubic octahedra,

---

the solubility of which in water at various temperatures is as follows ¹:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams K₂PtCl₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>per 100 grams</td>
</tr>
</tbody>
</table>

Potassium Chlor-platinate, K₂PtCl₄, is most readily obtained by adding potassium chloride to an acidulated solution of platinum tetrachloride. It crystallises in cubic octahedra which are yellow in colour and but slightly soluble in water, and still less soluble in alcohol. The formation of this salt is therefore utilised in the quantitative estimation of potassium and platinum.

Its solubility in water at various temperatures is as follows ²:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>6·8</th>
<th>13·8</th>
<th>46·5</th>
<th>71</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams K₂PtCl₄ in 100 grams H₂O</td>
<td>0·724</td>
<td>0·878</td>
<td>0·927</td>
<td>1·776</td>
<td>3·018</td>
<td>5·23</td>
</tr>
</tbody>
</table>

The heat of formation of potassium chlor-platinate is ³:

\[ [\text{Pt}] + 2(\text{Cl}_2) + 2\text{KCl.} \text{Aq.} = K_2\text{PtCl}_4.\text{Aq.} + 58·3 \text{ Cals.} \]

When ignited, the salt decomposes, yielding a mixture of spongy platinum and potassium chloride. The reaction is not readily completed in air, but in a current of hydrogen the decomposition is quantitatively exact. The density of potassium chlor-platinate is 3·499.⁴

Rubidium Chlor-platinate, Rb₂PtCl₄, yields microscopic octahedral crystals, yellow in colour, and having the following solubilities in water at various temperatures ⁵:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grams Rb₂PtCl₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>per 100 grams</td>
</tr>
</tbody>
</table>

Silver Chlor-platinate, Ag₂PtCl₄, is obtained as a yellow precipitate by adding silver nitrate in excess to a cold solution of chlor-platinic acid. It is not quite pure, since it is slowly decomposed even by cold water, yielding silver chloride and a solution of platinum tetrachloride,⁶ which is dihydroxy-tetrachlor-platinic acid, PtCl₄.2H₂O or H₂PtCl₄(OH)₂.

Upon filtering off the silver chloride and concentrating the solution over sulphuric acid, the pentahydrate, PtCl₄.5H₂O, crystallises out. On warming, however, with excess of silver nitrate, the silver salt of dihydroxy-tetrachlor-platinic acid is obtained, thus:

\[
\begin{align*}
\text{H}_2\text{PtCl}_6 + 2\text{AgNO}_3 &= \text{Ag}_2\text{PtCl}_4 + 2\text{HNO}_3 \\
\text{Ag}_2\text{PtCl}_4 + 2\text{H}_2\text{O} &= 2\text{AgCl} + \text{PtCl}_4.2\text{H}_2\text{O} \\
\text{PtCl}_4.2\text{H}_2\text{O} + 2\text{AgNO}_3 &= \text{Ag}_2\text{PtCl}_4(\text{OH})_2 + 2\text{HNO}_3.
\end{align*}
\]

The heat of formation of silver chlor-platinate is as follows ³:

\[ [\text{PtCl}_4] + 2[\text{AgCl}] = [\text{Ag}_2\text{PtCl}_4] + 7·7 \text{ Cals.} \]

¹ Seidell, *Solubilities of Inorganic and Organic Substances* (Crosby Lockwood, 1907).
⁶ Seidell, *opus cit.*
Group II.—Hexahydrated Salts

Sodium Chlor-platinate, \( \text{Na}_2\text{PtCl}_6.6\text{H}_2\text{O} \), crystallises in red, triclinic prisms, of density 2.499. These become anhydrous at 100°C., being converted into a yellow powder.\(^1\)

The heat of solution of the anhydrous salt is \(^2\):

\[
[\text{Na}_2\text{PtCl}_6] + \text{aq.} = \text{Na}_2\text{PtCl}_6.\text{aq.} + 8.54 \text{ Cals.}
\]

For the hydrated salt:

\[
[\text{Na}_2\text{PtCl}_6.6\text{H}_2\text{O}] + \text{aq.} = \text{Na}_2\text{PtCl}_6.\text{aq.} - 10.63 \text{ Cals.}
\]

The heat of formation is:

\[
[\text{Pt} + 2(\text{Cl}_2) + 2[\text{NaCl}] = [\text{Na}_2\text{PtCl}_6] + 78.7 \text{ Cals.}
\]

In addition to the foregoing the chlor-platinates of the following metals have been prepared:

- Barium,\(^8\) \( \text{BaPtCl}_6.6\text{H}_2\text{O} \);
- Cadmium,\(^9\) \( \text{CdPtCl}_6.6\text{H}_2\text{O} \);
- Cobalt,\(^3\) \( \text{CoPtCl}_6.6\text{H}_2\text{O} \);
- Copper (ferrous),\(^3\) \( \text{FePtCl}_6.6\text{H}_2\text{O} \);
- Lithium,\(^4\) \( \text{Li}_{2}\text{PtCl}_6.6\text{H}_2\text{O} \);
- Magnesium,\(^5\) \( \text{MgPtCl}_6.6\text{H}_2\text{O} \);
- Manganese,\(^5\) \( \text{MnPtCl}_6.6\text{H}_2\text{O} \);
- Nickel,\(^6\) \( \text{NiPtCl}_6.6\text{H}_2\text{O} \);
- Thallium,\(^7\) \( \text{Tl}_2\text{PtCl}_6.6\text{H}_2\text{O} \); and
- Zinc,\(^7\) \( \text{ZnPtCl}_6.6\text{H}_2\text{O} \).

Group III.—Salts containing varying quantities of Combined Water

The chlor-platinates of:

- Aluminium,\(^5\) \( \text{AlCl}_3.\text{PtCl}_4.15\text{H}_2\text{O} \);
- Calcium,\(^3\) \( \text{CaPtCl}_6.8\text{(or 9)}\text{H}_2\text{O} \);
- Cerium,\(^6\) \( \text{CeCl}_3.\text{PtCl}_4.13\text{H}_2\text{O} \) and \(^7\) \( 4\text{CeCl}_3.8\text{PtCl}_4.24\text{H}_2\text{O} \);
- Gadolinium,\(^8\) \( \text{GdCl}_3.\text{PtCl}_4.10\text{H}_2\text{O} \);
- Glucinium,\(^9\) \( \text{GdPtCl}_6.8\text{H}_2\text{O} \);
- Indium,\(^10\) \( 2\text{InCl}_3.5\text{PtCl}_4.36\text{H}_2\text{O} \);
- Iron (ferric),\(^10\) \( 2\text{FeCl}_3.2\text{PtCl}_4.21\text{H}_2\text{O} \);
- Lead,\(^11\) \( \text{PbPtCl}_6.8\text{(or 4)}\text{H}_2\text{O} \);
- Strontium,\(^3\) \( \text{SrPtCl}_6.8\text{H}_2\text{O} \);
- Tin (stannic),\(^10\) \( \text{SnCl}_4.\text{PtCl}_4.12\text{H}_2\text{O} \); and
- Zirconyl,\(^10\) \( \text{ZrO.PtCl}_6.12\text{H}_2\text{O} \).

\(^2\) Thomsen, *J. prakt. Chem.*, 1878, [ii], 18, 38.
\(^5\) Welkow, *Ber.*, 1874, 7, 304.
\(^6\) Bohn, *Bull. Soc. chim.*, 1874, [ii], 21, 534; Cleve, *ibid.*, 1874, [ii], 21, 118, 197, 247, 345; *Compt. rend.*, 1880, 91, 331.
\(^7\) Holtzmann, *J. prakt. Chem.*, 1881, [i], 84, 76.
\(^8\) Benedicks, *Zeitsch. anorg. Chem.*, 1900, 22, 393.
\(^9\) Thomsen, *Ber.*, 1870, 3, 827; 1874, 7, 75; Welkow, *Ber.*, 1873, 6, 1288.
\(^10\) Nilson, *Bull. Soc. chim.*, 1877, [ii], 27, 206.
Chlor-hydroxy-platinic Acids, \( \text{H}_2\text{PtCl}_6 \cdot n(\text{OH})_n \).

**Pentachlor-hydroxy-platinic Acid**, \( \text{H}_2\text{PtCl}_5(\text{OH})_4 \).—The monohydrate of this acid, namely, \( \text{H}_2\text{PtCl}_5(\text{OH}) \cdot \text{H}_2\text{O} \), is obtained \(^1\) as a deliquescent residue on keeping crystals of hexachlor-platinic acid in a vacuum over caustic potash at 100°C. for three days:

\[
\text{H}_2\text{PtCl}_5 \cdot 6\text{H}_2\text{O} = \text{H}_2\text{PtCl}_5(\text{OH}) \cdot \text{H}_2\text{O} + \text{HCl} + 4\text{H}_2\text{O}.
\]

It readily dissolves in water, yielding a yellow solution with an acid reaction, sufficiently powerful to decompose carbonates.\(^2\) With ammonia no precipitate is obtained, which property serves to distinguish this acid from hexachlor-platinic acid. With ammonium chloride or potassium chloride the corresponding hexachlor-platinate is produced.

Titration with alkali, using phenolphthalein as indicator, shows that the acid is dibasic,\(^3\) and several salts have been prepared. Of these the best known are:

**Barium Pentachlor-hydroxy-platinate**, \( \text{BaPtCl}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O} \), which is prepared by neutralising a solution of the acid with baryta water. On concentration in a desiccator the salt crystallises out in orange-yellow prisms.\(^4\)

**Silver Pentachlor-hydroxy-platinate**, \( \text{Ag}_2\text{PtCl}_6(\text{OH})_2 \), which results as a yellow precipitate \(^4\) on adding a solution of silver nitrate to the acid.

**Strontium, Thallium, and Lead** salts, namely, \( \text{SrPtCl}_5(\text{OH}) \cdot \text{H}_2\text{O} \), \( \text{Tl}_2\text{PtCl}_5(\text{OH})_4 \), and \( \text{PbPtCl}_5(\text{OH})_2 \cdot \text{Pb(OH)}_2 \), have also been isolated, and evidence has been obtained of the possibility of the existence of the sodium salt, \( \text{Na}_2\text{PtCl}_5(\text{OH}) \), in solution.\(^4\)

**Tetrachlor-dihydroxy-platinic Acid**, \( \text{H}_2\text{PtCl}_4(\text{OH})_2 \) or \( \text{PtCl}_4 \cdot 2\text{H}_2\text{O} \), is obtained in solution by hydrolysing silver hexachlor-platinate with boiling water:

\[
\text{Ag}_2\text{PtCl}_6 + 2\text{H}_2\text{O} = 2\text{AgCl} + \text{H}_2\text{PtCl}_4(\text{OH})_2.
\]

and exists in solution when platinum tetrachloride is dissolved in water.

Upon concentrating the solution and heating the residue to 100°C. the monohydrate of platinic chloride, \( \text{PtCl}_4 \cdot \text{H}_2\text{O} \), is obtained. Further dehydration cannot be effected in this manner without decomposition of the salt.

The solution has an acid reaction, decomposing carbonates. Titration with alkali, using phenolphthalein as indicator, shows that the acid is dibasic.

Several salts of this acid have been prepared. The silver salt, \( \text{Ag}_2\text{PtCl}_6(\text{OH})_2 \), has long been known. Other salts are\(^4\) those of **zinc**, \( \text{ZnPtCl}_4(\text{OH})_2 \cdot 3\text{H}_2\text{O} \); **cadmium**, \( \text{CdPtCl}_4(\text{OH})_2 \); **lead**, \( \text{PbPtCl}_4(\text{OH})_2 \), and a basic lead salt, \( \text{PbPtCl}_4(\text{OH})_2 \cdot \text{Pb(OH)}_2 \).

**Dichlor-tetrahydroxy-platinic Acid**, \( \text{H}_2\text{PtCl}_4(\text{OH})_4 \), is readily obtained in aqueous solution by hydrolysing silver tetrachlor-dihydroxy-

---


\(^5\) Norton, *J. prakt. Chem.*, 1870, [ii], 2, 469; 1872, [ii], 5, 365; Jörgensen, *ibid.*, 1877, [ii], 16, 345.
platinate, \( \text{Ag}_2\text{PtCl}_4(\text{OH})_2 \), with water at 100° C. The reaction takes several hours to complete, but proceeds as follows 1:

\[
\text{Ag}_2\text{PtCl}_4(\text{OH})_2 + 2\text{H}_2\text{O} = 2\text{AgCl} + \text{H}_2\text{PtCl}_2(\text{OH})_4.
\]

The acid is also produced when ammonium hydroxide is added in the requisite amount to a solution of the tetrachlor-dihydroxy acid:

\[
2\text{H}_2\text{PtCl}_4(\text{OH})_2 + 2\text{NH}_4\text{OH} = (\text{NH}_4)_2\text{PtCl}_6 + 2\text{H}_2\text{O} + \text{H}_2\text{PtCl}_2(\text{OH})_4.
\]

The solution is evaporated to dryness and the acid extracted with water, ammonium hexachlor-platinate remaining behind as an insoluble residue.

When mixed with excess of dilute hydrochloric acid, hexahydroxy-platinic acid dissolves, yielding the dichlor-tetrahydroxy acid.

When diluted with water this acid yields the hexahydroxy acid in amorphous form, but in a crystalline form if dialysed. 2

If an excess of ammonium hydroxide is added to a solution of the tetrahydroxy acid the liquid darkens and ultimately deposits a brown flocculent mass of **Fulminating Platinum,** \( \text{NH}_3\text{Pt}_2(\text{OH})_{10} \), which is soluble in dilute hydrochloric acid. The flocculent mass resembles hydrated ferric oxide in appearance and contains no chlorine. If dried at 100° C. after thorough washing, and then exposed to further desiccation over sulphuric acid, it absorbs moisture upon exposure to air with such avidity that the particles jump about.

When gently warmed to 125° C. the substance darkens in colour and loses the equivalent of a molecule of water. At 180° C. it becomes black, and above 250° C. it decomposes with violent detonation, nitrogen, water vapour, and oxygen being evolved, and a residue of platinum sponge remaining behind.

If pyridine is added to dichlor-tetrahydroxy-platinic acid instead of ammonia, a similar detonating product is obtained, presumably having an analogous composition, namely, \( \text{C}_2\text{H}_5\text{N.Pt}_2(\text{OH})_{10} \).

**Monochlor-pentahydroxy-platinic Acid,** \( \text{H}_2\text{PtCl}(\text{OH})_5 \), is obtained by the action of dilute sulphuric acid upon the barium salt. It is a brown, deliquescent syrup. It is dibasic in character. Its solutions decompose carbonates, slowly in the cold, but readily on warming.

The calcium salt is obtained by the action of sunlight on chlor-platinic acid in the presence of lime. 3 The barium and strontium salts have likewise been obtained in a similar manner. If alkali hydroxides are employed, however, instead of the alkaline earths, similar salts are not obtained.

**PLATINUM AND BROMINE**

- **Platinous Bromide, Platinum Dibromide,** \( \text{PtBr}_3 \), results as a brown, insoluble powder on heating brom-platinic acid, \( \text{H}_2\text{PtBr}_3 \), in air at about 280° C. 4

**Brom-platinous Acid,** \( \text{H}_2\text{PtBr}_4 \), has not been isolated in the pure

---

state, but exists in solution when platinous bromide is dissolved in aqueous hydrogen bromide. It combines with bases to form:

\[ \text{Brom-platinites, } M_2\text{PtBr}_4 \]

Of these the most important salt is:

**Potassium Tetrabrom-platinite,** \( K_2\text{PtBr}_4 \cdot 2\text{H}_2\text{O} \), which may be obtained \(^1\) by reduction of the hexabrom-platinate, \( K_2\text{PtBr}_6 \), with potassium oxalate solution at 100° C., or by addition of sodium bromide to potassium tetrachlor-platinite. \(^2\)

On concentration, the brom-platinite crystallises out in large, black, rhombic crystals:

\[ a : b : c = 0.60582 : 1 : 0.70499. \]

The crystals are readily soluble in water. Their heat of formation is as follows \(^3\):

\[ [\text{Pt}] + \text{Br}_2 + 2\text{KBr.Aq.} = K_2\text{PtBr}_4 \cdot \text{Aq.} + 21.83 \text{ Cals.} \]

The heat of solution of the crystals is:

\[ [K_2\text{PtBr}_4] + \text{Aq.} = K_2\text{PtBr}_4 \cdot \text{Aq.} - 10.6 \text{ Cals.} \]

**Platinic Bromide, Platinum Tetrabromide,** \( \text{PtBr}_4 \).—This salt is obtained by maintaining brom-platinic acid at 180° C. in air. \(^4\) The product is not pure, for even at this temperature it undergoes partial dissociation into the dibromide \(^5\):

\[ \text{PtBr}_4 \rightleftharpoons \text{PtBr}_2 + \text{Br}_2. \]

As obtained in this way, platinic bromide is a dark powder, slightly soluble in water to a reddish brown solution which contains dihydroxy-tetrabrom-platinic acid, \( \text{H}_2\text{PtBr}_4(\text{OH})_2 \). It is fairly soluble in a mixture of alcohol and water, and very soluble both in alcohol and in ether. On warming, however, these latter solutions become reduced, yielding a deposit of platinum black. Its solution in aqueous hydrogen bromide contains brom-platinic acid.

The salt has not as yet been obtained in a perfectly pure condition. Its heat of formation is given by Pigeon \(^6\) :

\[ [\text{Pt}] + 2\text{Br}_2 = [\text{PtBr}_4] + 42.4 \text{ Cals.} \]
\[ [\text{Pt}] + 2(\text{Br}_2) = [\text{PtBr}_4] + 56.8 \text{ Cals.} \]

**Brom-platinic Acid,** \( \text{H}_2\text{PtBr}_6 \), was first obtained by Balard \(^7\) in a more or less pure condition by acting on platinum with a mixture of nitric and hydrobromic acids.

A more satisfactory method consists in dissolving platinum sponge in hydrobromic acid saturated with bromine. This may be effected in a sealed glass tube at 180° C., but that is not necessary. If the platinum sponge is simply boiled for a short time with an excess of bromine and hydrobromic acid in a flask with a reflux condenser, the whole is dissolved, \(^8\) yielding a solution of brom-platinic acid.

---

\(^1\) Büllmann and Anderson, *Ber.*, 1903, 36, 1565.


\(^3\) Thomsen, *loc. cit.*, p. 436.


\(^5\) Gutbier and Blumer, *Zeits. anorg. Chem.*, 1913, 81, 381.


Gutbier prepared pure brom-platinic acid by repeatedly evaporating the pure chloride with concentrated hydrobromic acid on the water-bath and then treating it similarly three or four times with hydrobromic acid containing bromine. The residue, on being taken up with dilute hydrobromic acid, yields a deep carmine-red solution.

Brom-platinic acid crystallises in red, monoclinic prisms, containing 9 molecules of water, thus: \( \text{H}_2\text{PtBr}_6 \cdot 9\text{H}_2\text{O} \). The crystals are deliquescent and readily soluble in water, alcohol, and ether. When heated in air up to 180° C. they melt, water and hydrogen bromide being evolved, platinic bromide constituting the residue.

The heat of formation is as follows:

\[
\text{[Pt]} + 2\text{Br}_2 + 2\text{HBr} \cdot \text{aq.} = \text{H}_2\text{PtBr}_6 \cdot \text{aq.} + 60.7 \text{ Cals.}
\]

Brom-platinic acid possesses a strongly acid character, decomposing carbonates and uniting with bases generally, to form salts known as:

**Brom-platinates, M\(_2\)PtBr\(_6\).**

These salts are isomorphous with the chlor-platinates already described, and which they resemble in their general chemical reactions. The alkali salts are best known, and are readily prepared by addition of a solution of the alkali bromide to one of brom-platinic acid, and crystallising the precipitated complex from dilute hydrobromic acid.3

The solubilities of the alkali brom-platinates in water and dilute hydrobromic acid decrease with increasing atomic weight of the alkali metal. The solutions obtained are red in colour, but turn yellow on dilution with water. Hydrazine hydrate decomposes them with ease, metallic platinum being deposited and nitrogen evolved.

Numerous brom-platinates of organic bases have been prepared and described,4 but to deal with these is beyond the scope of this work. The more important inorganic brom-platinates are as follow:

**Ammonium Brom-platinate**, \((\text{NH}_4)_2\text{PtBr}_6\), crystallises in cubic octahedra, which are dark brown in colour5 and isomorphous with the corresponding potassium salt.

When heated, ammonium brom-platinate decomposes, partly according to the equation

\[
3(\text{NH}_4)_2\text{PtBr}_6 = 3\text{Pt} + 16\text{HBr} + 2\text{NH}_4\text{Br} + 2\text{N}_2,
\]

and partly

\[
(\text{NH}_4)_2\text{PtBr}_6 = \text{Pt} + 2\text{NH}_4\text{Br} + 2\text{Br}_2.
\]

By thorough drying of the salt, however, the quantity of bromine liberated is reduced.6

The density of the salt is 4.265.7 It dissolves in water to a deep orange-red solution, which, when saturated at 20° C., contains 0.59 grams of \((\text{NH}_4)_2\text{PtBr}_6\) per 100 grams of solution.8

---

6 Halberstadt, *Ber.*, 1884, 17, 2962.
Caesium Brom-platinate, $\text{Cs}_2\text{PtBr}_8$, crystallises in reddish yellow octahedra.\(^1\)

Potassium Brom-platinate, $\text{K}_2\text{PtBr}_6$, results as dark brown octahedra, from which it is difficult to remove all traces of water.\(^1\) The crystals are not very soluble, a solution saturated at the ordinary temperature containing 2.02 per cent. of its weight of the salt.\(^2\) At 100° C, the salt dissolves in 10 times its weight of water. The density of the crystals is 4.658.\(^3\)

The heat of formation is \(^4\):

$$[\text{Pt}] + 2(\text{Br}_2) + 2\text{KBr} \cdot \text{Aq.} = \text{K}_2\text{PtBr}_6 \cdot \text{Aq.} + 59.3 \text{ Cals.}$$

The heat of solution is:

$$[\text{K}_2\text{PtBr}_6] + \text{Aq.} = \text{K}_2\text{PtBr}_6 \cdot \text{Aq.} - 12.2 \text{ Cals.}$$

Rubidium Brom-platinate, $\text{Rb}_2\text{PtBr}_6$, yields reddish yellow octahedra. The salt retains traces of moisture most obstinately.\(^1\)

Sodium Brom-platinate, $\text{Na}_2\text{PtBr}_6 \cdot 6\text{H}_2\text{O}$, yields deep red, triclinic prisms, isomorphous with those of sodium chlor-platinate hexahydrate. The salt is readily soluble in water, stable in air, and has a density of 3.823.\(^5\)

Brom-platinates \(^6\) of:

Barium, $\text{BaPtBr}_6 \cdot 10\text{H}_2\text{O}$;
Calcium, $\text{CaPtBr}_6 \cdot 12\text{H}_2\text{O}$;
Cobalt, $\text{CoPtBr}_6 \cdot 12\text{H}_2\text{O}$;
Copper, $\text{CuPtBr}_6 \cdot 8\text{H}_2\text{O}$;
Lead, $\text{PbPtBr}_6$;
Magnesium, $\text{MgPtBr}_6 \cdot 12\text{H}_2\text{O}$;
Manganese, $\text{MnPtBr}_6 \cdot 12\text{H}_2\text{O}$;
Nickel, $\text{NiPtBr}_6 \cdot 6\text{H}_2\text{O}$;
Silver, $\text{Ag}_3\text{PtBr}_6$;
Strontium, $\text{SrPtBr}_6 \cdot 10\text{H}_2\text{O}$; and
Zinc, $\text{ZnPtBr}_6 \cdot 12\text{H}_2\text{O}$, have been described.

Tetrabrom-dihydroxy-platinic Acid, $\text{H}_2\text{PtBr}_4(\text{OH})_2$. — Platinum tetrabromide is only slightly soluble in water, yielding a reddish brown solution containing the dihydroxy acid. With silver nitrate the acid solution yields a dark brown precipitate of the silver salt,\(^7\) $\text{Ag}_2\text{PtBr}_4(\text{OH})_2$.

In an analogous manner salts of lead, $\text{PbPtBr}_4(\text{OH})_2 \cdot \text{Pb}(\text{OH})_2$; thallium, $\text{Tl}_2\text{PtBr}_4(\text{OH})_2$; and mercury, $\text{HgPtBr}_4(\text{OH})_2$, have been prepared,\(^7\) whilst electric conductivity measurements indicate that the sodium salt, $\text{Na}_2\text{PtBr}_4(\text{OH})_2$, can exist in solution.\(^7\)

---

2 Halberstadt, *Ber.*, 1884, 17, 2962.
PLATINUM AND IODINE

Platinous Iodide, Platinum Di-iodide, PtI₂, may be obtained by warming a solution of potassium iodide with platinous chloride. The method is not altogether satisfactory because of the difficulty of deciding when the reaction is complete. If the heating is too prolonged the platinous iodide is converted into the platinic salt, PtI₂, and free platinum, the former of which passes into solution, whilst the latter contaminates the deposited di-iodide. On the other hand, if the reaction is not carried to completion the product is mixed with unattacked dichloride.

As prepared by the foregoing method, however, platinum di-iodide is obtained as a black, insoluble powder, stable in air. It is slowly soluble in hydriodic acid, but the solution undergoes decomposition into the tetra-iodide and metallic platinum. When heated to about 300° or 350° C. it dissociates into its components.

Platinic Iodide, Platinum Tetra-iodide, PtI₄, is readily prepared in a variety of ways. It is deposited on addition of hydriodic acid, or of sodium (or potassium) iodide to a warm solution of chlor-platinic acid, and allowing to stand at the ordinary temperature. The solution becomes turbid and finally deposits crystals of iodide.

The salt may also be obtained by direct union of the components, as, for example, by heating finely divided platinum and iodine in sealed tubes. It results when iodo-platinic acid is heated to 100° C., and when platinum sponge is dissolved in a solution of iodine in aqueous hydriodic acid. The dark red solution is evaporated to dryness, raised to 180° C., and washed with boiling water.

Platinic iodide is a blackish brown, amorphous powder, which evolves iodine vapour when placed in vacuo even at ordinary temperatures. When warmed to 180° C. in air, iodine is evolved.

The heat of formation of platinic iodide solution is given as:

\[
\begin{align*}
[\text{Pt}] + 2[I\text{₂}] &= [\text{PtI}_4] + 17.4 \text{ Cals.} \\
[\text{Pt}] + 2(I\text{₂}) &= [\text{PtI}_4] + 39.0 \text{ Cals.}
\end{align*}
\]

Although insoluble in water, platinic iodide dissolves in alcohol. Its molecular conductivity in ethyl alcohol at 25° C. increases with dilution until the concentration has been reduced to 0.25 gram molecule in 600 litres, when it becomes constant.

Iodo-platinic Acid, \(\text{H}_2\text{PtI}_₄\cdot 9\text{H}_₂\text{O}\).—This acid exists in solution when platinum tetra-iodide is dissolved in aqueous hydriodic acid. Upon concentration it separates out in reddish black, monoclinic crystals. These are easily soluble in water; they deliquesce upon exposure to air, whilst in vacuo they lose hydrogen iodide. When heated to 100° C. platinum tetra-iodide is obtained.

The aqueous solution is unstable, a deposit of the tetra-iodide

---

2 Topsoe, Jahresber., 1870, p. 388.
4 Clementi, Nuovo Cimento, 1855, 2, 192.
being obtained on prolonged standing, particularly with exposure to sunlight.

**Hexas-iodo-platinates, \( M_2PtI_6 \)**

Iodo-platinic acid unites with bases to form salts of general formula \( M_2PtI_6 \). Those of the alkali metals are mostly anhydrous and isomorphous with the corresponding chlor-platinates and brom-platinates.

The iodo-platinates of zinc, magnesium, etc., crystallise with 9 molecules of water, and form an isomorphous series of their own.

The iodo-platinates may be prepared by dissolving either platinum tetra-iodide or chlor-platinic acid in aqueous solutions of the iodides of the metals; and by neutralisation of the hydroxides of the metals with iodo-platinic acid.

**The Alkali Iodo-platinates, \( M_2PtI_6 \)**

Ammonium Iodo-platinate, \((NH_4)_2PtI_6\), crystallises in cubo-octahedra having a black colour and a metallic lustre. The solution is unstable, a deposit of platinum tetra-iodide being obtained on standing.\(^1\)

Potassium Iodo-platinate, \(K_2PtI_6\), crystallises in black cubes having a metallic lustre. It readily dissolves in water, yielding a wine-red solution. When dilute, the solution is not stable, a deposit of platinum tetra-iodide being obtained on prolonged standing.\(^2\)

Sodium Iodo-platinate, \(Na_2PtI_6\cdot6H_2O\), crystallises in greyish blue, deliquescent needles \(^3\) belonging to the monoclinic system.\(^4\)

**Iodo-platinates of Divalent Metals, \( RPtI_6\cdot xH_2O \)**

The iodo-platinates of the following metals have been prepared:

- **Barium**, \( BaPtI_6\cdot xH_2O \);
- **Calcium**, \( CaPtI_6\cdot12H_2O \);
- **Cobalt**, \( CoPtI_6\cdot9H_2O \);
- **Iron (ferrous)**, \( FePtI_6\cdot9H_2O \);
- **Magnesium**, \( MgPtI_6\cdot9H_2O \);
- **Manganese**, \( MnPtI_6\cdot9H_2O \);
- **Nickel**, \( NiPtI_6\cdot9H_2O \); and
- **Zinc**, \( ZnPtI_6\cdot9H_2O \).

**Tetra-iodo-dihydroxy-platinic Acid, \( H_2PtI_4(OH)_2 \)**, has been obtained by Bellucci \(^5\) in solution as the result of allowing platinum tetra-iodide to remain in contact with 95 per cent. alcohol. The brown solution obtained has an acid reaction, and decomposes carbonates.

By addition of concentrated aqueous solutions of soluble salts of **silver**, **lead**, **thallium**, and **mercury**, the following insoluble salts have been obtained: \( Ag_2PtI_4(OH)_2 \); \( PbPtI_4(OH)_2\cdot Pb(OH)_2 \); \( Tl_2PtI_4(OH)_2 \); and \( HgPtI_4(OH)_2 \).

**Platinum Chlor-iodide, \( PtCl_2I_2 \)**, is described \(^6\) as yielding brick-red, deliquescent prisms when platinum is dissolved in aqua regia in the presence of iodine.

**Mixed Halogen Platinates** have been prepared, such as, for example,
Potassium tetrachloro-dibromo-platinate, $\text{K}_2\text{PtCl}_5\text{Br}_2$, which results on adding potassium bromide to an aqueous solution of tetrachloro-platinitic acid.\(^1\) It yields octahedral crystals.

The remaining members of the series, namely, $\text{K}_2\text{PtCl}_5\text{Br}$; $\text{K}_2\text{PtCl}_4\text{Br}_3$; $\text{K}_2\text{PtCl}_4\text{Br}_4$; and $\text{K}_2\text{PtClBr}_3$; have also been prepared.

**PLATINUM AND OXYGEN**

**Platinous Oxide, Platinum Monoxide,** $\text{PtO}$, is produced \(^2\) in the anhydrous condition in the form of superficial blackening when platinum, either in the form of sponge or of thin foil, is heated in dry oxygen at about 450° C., the product containing as much as 48 per cent. of oxide.

It dissolves in hydrochloric acid containing a trace of platinous chloride, yielding this latter salt.

When heated, platinous oxide decomposes, yielding metallic platinum and its dioxide.\(^3\)

**Hydrated Platinum Monoxide,** $\text{PtO\cdot}_2\text{H}_2\text{O}$, is obtained in a more or less impure condition by the addition of warm potassium hydroxide solution to platinous chloride.\(^4\) The pure hydrated oxide, however, may be obtained \(^5\) by boiling a solution of potassium chlor-platinite with the calculated amount of sodium hydroxide solution. The hydrated oxide separates out as a dark precipitate, which is readily oxidised by exposure to air, so that it is necessary to wash and dry it in an atmosphere of carbon dioxide. It retains its combined water very tenaciously, and cannot be completely dehydrated without partial decomposition.

The freshly precipitated oxide is soluble in concentrated hydrochloric acid and in sulphurous acid. Concentrated nitric and sulphuric acids also effect its solution, but the dilute acids are practically without action. After drying in an exsiccator, however, hydrated platinum monoxide is insoluble in concentrated sulphuric or nitric acid. It dissolves, however, in concentrated hydrochloric acid.

The hydrated oxide possesses oxidising powers, arsenious acid being oxidised to arsenic acid, hydrogen iodide to iodine, whilst hydrogen gas raises the oxide to incandescence, water being formed.

The oxide is capable also of effecting certain reductions, hydrogen peroxide being reduced to water, and acidulated potassium permanganate to manganese dioxide, platinum dioxide being simultaneously formed.

**Triplatinum Tetroxide,** $\text{Pt}_3\text{O}_4$—An oxide corresponding in empirical composition to $\text{Pt}_3\text{O}_4$ was described by Jörgensen,\(^6\) but appears \(^5\) to have been a mixture of monoxide and dioxide rather than a separate chemical entity.

**Hydrated Platinum Sesquioxide,** $\text{Pt}_2\text{O}_3\cdot_2\text{H}_2\text{O}$, may be obtained \(^7\) by decomposing the trichloride, $\text{PtCl}_3$, with a hot solution of sodium

---

COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

carbonate; it also results on acidifying with acetic acid a solution of the trichloride in potassium hydroxide solution.

Hydrated platinum sesquioxide is a brown substance, insoluble in water, but soluble both in concentrated sulphuric acid and in caustic alkali solutions. When dehydrated in vacuo, it decomposes, so that the anhydrous sesquioxide has not been obtained.

Hydrated Platinum Dioxide, PtO\(_2\).xH\(_2\)O, is obtained \(^1\) by boiling platinum tetrachloride with an excess of twice normal sodium hydroxide solution, and then neutralising with acetic acid. The precipitate obtained when the foregoing reactions are carried out in dilute solution, and when the acetic acid is added in the cold, consists of a white deposit of tetrahydrate, PtO\(_2\).4H\(_2\)O. Thishydrate is acid in character, and is probably more correctly represented by the formula H\(_2\)Pt(OH)\(_6\) and is described in further detail under the name of hexahydroxy-platinic acid (see below). It readily loses water, becoming yellow on drying in consequence of partial dehydration. When boiled with water the precipitated tetrahydrate becomes ochre-coloured, being transformed into the trihydrate, PtO\(_2\).3H\(_2\)O. Upon prolonged exposure to sulphuric acid in a desiccator further dehydration ensues, the yellowish brown dihydrate, PtO\(_2\).2H\(_2\)O, being produced. When maintained for some time at 100° C, the mass becomes black and resembles coal in appearance, but yields upon pulverisation a dark brown powder. This is the monohydrate, PtO\(_2\).H\(_2\)O, which clings tenaciously to its combined water. It is soluble with difficulty in hydrochloric acid, although, when a portion of the oxide has passed into solution, the remainder dissolves more rapidly on gentle shaking.

On saturating a solution of chlor-platinic acid with hexahydroxy-platinic acid and dialysing, a product is formed which coagulates on warming, and has a composition represented by the formula (PtO\(_2\)).2HCl.9H\(_2\)O. Boiling water converts it into metapluminic acid, (PtO\(_2\)).5H\(_2\)O.\(^2\)

When aqueous solutions of organic acids are boiled with the dioxide, reduction takes place, metallic platinum being deposited, and the acids oxidised. Hydrogen peroxide solution slowly reduces the dioxide.

Platinum dioxide, upon ignition, decomposes, evolving oxygen, a residue of metallic platinum being obtained together with a solid solution of either the monoxide or the sesquioxide in the dioxide.\(^3\)

Hexahydroxy-platinic Acid, H\(_2\)Pt(OH)\(_6\), or PtO\(_2\).4H\(_2\)O, is obtained as a white precipitate on neutralising with acetic acid in the cold a well-diluted solution of platinum tetrachloride which has been boiled with excess of caustic soda.

When freshly prepared it is readily soluble in dilute acids or alkalis. On drying it undergoes slight dehydration, becoming yellowish in colour.

On dissolving in dilute caustic alkalis it yields salts of the type M\(_2\)Pt(OH)\(_6\). The sodium and potassium salts of this acid have been prepared,\(^4\) and that these salts correspond to the foregoing formula and

\(^1\) Wöhler, Zeitsch. anorg. Chem., 1904, 40, 423; Beluccei, ibid., 1905, 44, 168. Unless the precautions enunciated by these authors are taken, the product is contaminated with alkali. The oxide obtained by early workers was impure. See Berzelius, Schweigger's J., 1813, 7, 55; Doebereiner, Pogg. Annalen, 1833, 28, 181; Annalen, 1836, 17, 67; Topsoe, Ber., 1870, 3, 462.


\(^3\) Wöhler and Frey, Zeitsch. Elektrochem., 1909, 15, 129.

\(^4\) Beluccei, Atti R., Accad. Lincei, 1903, [v], 12, ii, 635.
are not simply hydrates of the type $\text{M}_2\text{PtO}_3\cdot3\text{H}_2\text{O}$, is established, not only by their being stable at $100^\circ\text{C}$, but by their precipitating from aqueous silver acetate solution the salt $\text{Ag}_2\text{Pt(OH)}_6$, which is also stable at $100^\circ\text{C}$. In a similar manner thallium hexahydroxy-platinate, $\text{Tl}_2\text{Pt(OH)}_6$, may be thrown out of solution.

Still further evidence in favour of the correctness of the foregoing formula is afforded by the interesting isomorphism existing between potassium platinate and the stannate and plumbate of the same metal. This is evident from the crystallographic measurements detailed below.\(^1\)

The salts crystallise according to the rhombohedral system.

\[
\begin{align*}
K_2\text{Pt(OH)}_6 & : a : c = 1 : 1.9952 \quad \alpha = 69^\circ 11' 4'' \\
K_2\text{Pb(OH)}_6 & : a : c = 1 : 1.9514 \quad \alpha = 70^\circ 10' 26'' \\
K_2\text{Sn(OH)}_6 & : a : c = 1 : 1.9588 \quad \alpha = 70^\circ 0' 44''
\end{align*}
\]

Electric conductivity measurements indicate that potassium platinate undergoes normal dissociation in dilute aqueous solution like other salts of dibasic acids. It is not hydrolysed by water at $25^\circ\text{C}.\(^2\)

The sodium salt, $\text{Na}_2\text{Pt(OH)}_6$, after standing for several days becomes gelatinous owing to the separation of $\text{Na}_2\text{O}\cdot(\text{PtO}_2)_2\cdot6\text{H}_2\text{O}$, which, upon prolonged dialysis, yields $\text{Na}_2\text{O}\cdot(\text{PtO}_2)_2\cdot9\text{H}_2\text{O}.\(^3\)

When mixed with excess of dilute hydrochloric acid, hexahydroxy-platinic acid dissolves, yielding dichlor-tetrahydroxy-platinic acid, $\text{H}_2\text{PtCl}_4(\text{OH})_4$.

**Platinum Trioxide**, $\text{PtO}_3$, has been obtained\(^4\) by electrolysis a well-cooled solution of hydrated platinum dioxide in 2-Normal potassium hydroxide, using platinum electrodes. The anode becomes covered with an amorphous, golden-coloured film of potassium platinate, having the composition $K_2\text{O}\cdot\text{PtO}_3$ or $K_2\text{PtO}_4$. This, by treatment with ice-cold, dilute acetic acid, yields the free trioxide as a reddish brown substance, which gradually loses oxygen, but never becomes the pure dioxide on simply keeping in air, probably because a solid solution of trioxide in the dioxide is formed.

Platinum trioxide is not acted upon by dilute sulphuric, nitric, or acetic acid. Dilute hydrochloric acid dissolves it with evolution of chlorine, whilst sulphurous acid converts it into complex sulphites.

Concentrated hydrochloric acid rapidly dissolves the trioxide with violent chlorine evolution, whilst concentrated sulphuric and nitric acids slowly convert it into the dioxide in the warm.

When gently warmed oxygen is evolved, a residue of platinum dioxide being obtained.

A remarkable feature of the trioxide is the fact that it is not reduced by hydrogen peroxide, and Wöhler therefore regards it, not as a peroxide, but as the anhydride of platinic acid, in which the platinum is regarded as hexavalent, thus:

\[
\begin{align*}
\text{O} & \equiv \text{Pt} \left\langle \begin{array}{c} \text{O} \\
\text{O} \end{array} \right. 
\end{align*}
\]

It is suggested that the anodic passivity of platinum is attributable to the formation of a surface film of this oxide.

---


PLATINUM AND SULPHUR

Platinoic Sulphide, Platinum Monosulphide, PtS, was obtained by Davy by ignition of platinum sponge and sulphur in a closed tube. The product was a black, refractory mass.\(^1\)

Roessler\(^2\) obtained the sulphide by heating finely divided platinum with sulphur under a layer of borax. On extracting with hot water a dark, heavy powder remains.

Other methods consist in heating to white heat a mixture of platinum and pyrites under borax, a crystalline product being thereby obtained \(^3\); by heating in a closed crucible a mixture of ammonium chlor-platinate and sulphur \(^4\); and, finally, by the ignition of the oxysulphide, PtOS.\(\text{Aq.}\)\(^5\)

The product is a greyish black, insoluble substance, not attacked by acids or alkalies, and almost insoluble in aqua regia. When heated in a current of hydrogen it is readily reduced to the metal.

At high temperatures the sulphide apparently dissociates, leaving a residue of metallic platinum.

When hydrogen sulphide is passed into an aqueous solution of an alkali chlor-platinite, a black precipitate of the monosulphide is obtained.

Platinoic Sesquisulphide, Pt\(_2\)S\(_3\), is stated \(^6\) to result on oxidising—by exposure to air—thioplatinic acid, H\(_2\)Pt\(_4\)S\(_6\), obtained by the action of dilute hydrochloric acid upon potassium thioplatinate. Upon desiccation at 120° C. it is converted into a grey powder, of density 5.52.

It is readily reduced on warming in hydrogen, and when ignited in air the sulphur burns, leaving a residue of metallic platinum. Mineral acids do not attack the sulphide, and even aqua regia reacts but slowly upon it.

Platinoic Sulphide, Platinum Disulphide, PtS\(_2\), is obtained as a dark precipitate on passing hydrogen sulphide into an aqueous solution of platinum tetrachloride. It is necessary to effect the precipitation at about 90° C., otherwise coloured precipitates are obtained consisting most probably of thioplatinic acids.\(^7\)

Platinoic sulphide also results on heating chlor-platinic acid, decolorised by treatment with sulphur dioxide, to 200° C. in sealed tubes.\(^8\)

Obtained by either of these methods, platinum disulphide is a black deposit which readily oxidises in air, yielding an oxysulphide, PtOS.\(\text{xH}_2\text{O}\), and must therefore be dried in an atmosphere of an inert gas. If strongly heated in the last named it dissociates, platinum monosulphide resulting; but when ignited in air, it burns, leaving a residue of metallic platinum. Acids attack it with difficulty, and it is relatively insoluble in alkali sulphides.

A Polysulphide, of formula PtS\(_{18}\)(NH\(_4\))\(_2\),2H\(_2\)O, is described\(^9\) as resulting on addition of ammonium polysulphide to chlor-platinic acid. It yields large, red, rhombic crystals which, when dry, are stable.

1 Davy, Phil. Mag., 1812, 40, 27, 209, 350.
3 Deville and Debray, Compt. rend., 1879, 89, 597.
5 Böttger, J. prak. Chem., 1834, [1], 3, 274.
7 Antony and Lucchesi, Gazetta, 1896, 26, 211.
8 Geitner, Annalen, 1864, 129, 358.
9 A. Hofmann and Höchtl, Ber., 1903, 36, 3090.
Thio-platinates

The two sulphides of platinum unite with sulphides of the alkali metals to yield complex substances known as thio-platinates. These were studied mainly by Schneider,¹ who divided them into two groups, represented respectively by the general formulæ $M_2Pt_2S_6$ and $M_4Pt_3S_8$.

Group I.—$M_2S.3PtS.PtS_2$ or $M_2Pt_3S_6$

Potassium Thio-platinate, $K_2Pt_2S_6$, is a crystalline powder obtained by heating together platinum sponge and six times its weight of a mixture of equal parts of sulphur and potassium carbonate. Density 6.44 at 15°C.

The Sodium salt, Na$_2$Pt$_2S_6$, has also been described.

Group II.—$2M_2S.2PtS.PtS_2$ or $M_4Pt_3S_6$

The Sodium salt, Na$_2$Pt$_3S_6$, is described² as resulting on fusing a mixture of platinum sponge with twelve times its weight of an equal mixture of sodium carbonate and sulphur. It yields red copper-coloured needles which are unstable in air. When boiled with water they decompose, leaving an insoluble residue of Na$_2$Pt$_3S_6$.

Alkali Thio-stanno-platinates have also been described.³

Platinum Oxysulphide, PtOS.$x$H$_2$O, is obtained by allowing the di-sulphide in the wet condition to oxidise by exposure to air at about 70°C. with frequent stirring. The product is washed free from sulphuric acid, and dried at 100°C., when it results as a black powder. It is a powerful oxidiser, effecting the oxidation of hydrogen, hydrogen sulphide and of sulphur dioxide in the cold. Ferrous salts are oxidised by it, on warming, to the ferric condition, and oxalic acid to carbon dioxide.

Platinum Sulphite.—When sulphur dioxide is passed into an aqueous suspension of hydrated platinum dioxide, a colourless solution is obtained, from which, however, it does not seem possible to obtain the sulphite in a definite form.⁴

Numerous double sulphites and double chlor-sulphites of platinum and the alkali metals have, however, been described.⁴ For details of these the reader is referred to the accompanying references.

Platinitic Sulphate, Platinum Disulphate, Pt(SO$_4$)$_2$—Platinum sponge dissolves in concentrated sulphuric acid at about 350°C., and the solution assumes a yellow colour in consequence of the solution of platinum disulphate, Pt(SO$_4$)$_2$.⁵

The tetrahydrate, Pt(SO$_4$)$_2$.4H$_2$O, is deposited from solution ⁶ when an alternating current is passed through platinum electrodes immersed in sulphuric acid of density 1.840. On repeated recrystallisation from

¹ Schneider, Pogg. Annalen, 1869, 136, 105; 1869, 138, 604; J. prakt. Chem., 1874, [II], 8, 29; 1893, [II], 48, 411.
³ See Litton and Schnedermann, Annalen, 1842, 42, 316; Lang, J. prakt. Chem., 1861, [I], 83, 415; Schottländer, Annalen, 1866, 140, 200; Birnbaum, Annalen, 1866, 139, 164; 1869, 152, 137; 1871, 159, 116.
⁴ See Liebig, Annalen, 1857, 23, 23; Lang, J. prakt. Chem., 1861, [I], 83, 415; Birnbaum, Annalen, 1866, 139, 164; 1869, 152, 137; 1871, 159, 116.
⁵ Delépine, Compt. rend., 1905, 147, 1013.
⁶ Stucklik, Ber., 1894, 37, 2913; Margules, Wied. Annalen, 1898, 65, 629; 1898, 66, 540.
water in vacuo, the salt is obtained in the form of large, orange leaflets. These are very stable so long as they contain a trace of free sulphuric acid; but when quite pure they lose water upon prolonged exposure in a desiccator, yielding the anhydrous salt in the form of pretty crystals, exhibiting a green metallic reflex.

Both salts are soluble in water, the hydrated one yielding a yellow solution which deposits a brown basic salt on warming.

**Basic Sulphates.**—Hydrated platinum dioxide dissolves slowly in 50 per cent. sulphuric acid, and from the solution a basic sulphate, \( \text{Pt}_2\text{O}_2\cdot\text{SO}_3\cdot4\text{H}_2\text{O} \) or \( \text{Pt(OH)}_4\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O} \), separates out in orange-yellow microscopic needles on addition of excess of acid in the cold. The salt is hydrolysed by water. Heated to 100° C. three molecules of water are lost, the residue having the composition \( \text{PtO}_2\cdot\text{H}_2\text{SO}_4 \) or \( \text{H}_2\text{PtO}_2\cdot\text{SO}_4 \).

When dissolved in sulphuric acid, platinic sulphate is reduced by oxalic acid, yielding a complex sulphate of trivalent platinum, namely, \( \text{Pt}_2(\text{OH})_6\cdot(\text{SO}_3)_4\cdot(\text{OH})_2\cdot8\cdot5\text{H}_2\text{O} \). This yields well-defined triclinic prisms which gradually lose water when dried over sulphuric acid under reduced pressure, yielding a stable complex, \( \text{Pt}_2\text{O}_3\cdot(\text{SO}_3)_3\cdot\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O} \). This acid is dibasic, and yields crystalline potassium, sodium, and barium salts.\(^1\)

**PLATINUM AND SELENIUM**

**Platinoous Selenide, Platinum Monoselenide**, \( \text{PtSe} \).—Berzelius observed that platinum and selenium unite, when heated together, to yield a grey, refractory selenide. Roessler \(^2\) obtained the monoselenide by igniting an intimate mixture of platinum powder and half its weight of selenium under a layer of borax at a temperature approaching the melting-point of gold (circa 1062° C.).

The product is a dark grey, brittle substance, breaking up into shining leaflets when struck slightly.

With selenides of the alkali metals and of tin, complex seleno-stannopolatinates have been obtained. The general formula \( \text{M}_2\text{Se} \cdot \text{SnSe}_2 \cdot 3\text{PtSe} \) or \( \text{M}_2\text{SnPt}_3\text{Se}_6 \) is given to them, analogous to that for the thio-stannopolatinates, \( \text{M}_2\text{SnPt}_3\text{Se}_6 \).

**Platinum Triselenide**, \( \text{PtSe}_3 \), has been obtained as a black, flocculent precipitate by reduction with formaldehyde of a solution of an alkali chlor-platinate in the presence of a selenite and an excess of alkali.\(^3\)

The reaction may be represented as follows:

\[
\text{K}_2\text{PtCl}_6 + 8\text{SeO}_3 + 8\text{HCHO} + 12\text{KOH} = \text{PtSe}_3 + 6\text{KCl} + 8\text{HCOOK} + 10\text{H}_2\text{O}.
\]

Upon heating to dull redness in a current of carbon dioxide, platinum triselenide is converted into the *diselenide*, \( \text{PtSe}_2 \), which is left as a greyish black powder.

**PLATINUM AND TELLURIUM**

**Platinum Subtelluride**, \( \text{Pt}_2\text{Te} \).—On heating the monotelluride in the blowpipe for a short time a product \(^2\) is obtained corresponding to the formula \( \text{Pt}_2\text{Te} \).

---

Platinum Monotelluride, Pt\textsubscript{Te}.—On fusing the ditelluride in the blowpipe flame and then allowing it to cool, platinum monotelluride crystallises out in polyhedra.\textsuperscript{1}

It may also be obtained by heating an intimate mixture of finely divided tellurium (100 parts) and platinum (150 parts) in a glass tube until combination takes place. The tube and its molten contents are now melted together and dropped into cold water. The telluride then yields quite good crystals.

Platinum Ditelluride, Pt\textsubscript{Te}_\textsubscript{2}, results on heating an intimate mixture of finely divided platinum with a slight excess of tellurium above that theoretically required.\textsuperscript{2} The product is treated with concentrated potash solution to remove excess of tellurium, and the telluride remains as a grey, crystalline, insoluble powder.

When platinum is dissolved in a great excess of molten tellurium under borax and the mass allowed to cool slowly, the ditelluride crystallises out in octahedra and may be separated from the excess of tellurium by treatment with cold, dilute nitric acid.

Platinum ditelluride is but slowly attacked by boiling nitric acid, whilst boiling potash solution is without action upon it.

PLATINUM AND NITROGEN

Nitrosyl Derivatives.—On dissolving platinum in aqua regia a nitrosyl derivative, termed nitrosyl chlor-platinate, (NO\textsubscript{3})\textsubscript{2}PtCl\textsubscript{4} or PtCl\textsubscript{4}.2NOCl, is obtained along with more or less of hexachlor-platinic acid, H\textsubscript{2}PtCl\textsubscript{6}, according to circumstances.\textsuperscript{3} It is a brownish yellow, deliquescent substance, which dissolves in water, evolving nitrous fumes. When boiled with hydrochloric acid it decomposes, yielding chlor-platinic acid. Hence, in preparing this latter substance from scrap platinum for laboratory purposes, the solution of the metal in aqua regia is repeatedly evaporated to dryness and taken up with hydrochloric acid in order to ensure complete removal of this nitrosyl derivative.

Nitrosyl Brom-platinate, (NO\textsubscript{3})\textsubscript{2}PtBr\textsubscript{6}, is formed in an analogous manner to the preceding compound, namely, by dissolving platinum in a solution containing nitric and hydrobromic acids.

Tetranitroplatinites ro Platinonitrites, M\textsubscript{2}Pt(NO\textsubscript{3})\textsubscript{4}

Although platinum nitrite has not been isolated, double nitrites, of formula M\textsubscript{2}Pt(NO\textsubscript{3})\textsubscript{4}, analogous to the tetrachlorplatinites, M\textsubscript{2}PtCl\textsubscript{4}, are known. They are derived from Tetranitroplatinous Acid or Hydrogen Tetranitroplatinite, H\textsubscript{2}Pt(NO\textsubscript{3})\textsubscript{4}, which is obtained in solution on decomposing the barium salt with dilute sulphuric acid in the cold.\textsuperscript{3} On concentrating in vacuo, small red crystals are obtained which dissolve in water to yield a yellow, unstable solution. The most important salts of this acid are:

Ammonium Platinonitrite,\textsuperscript{3, 4} (NH\textsubscript{4})\textsubscript{2}Pt(NO\textsubscript{3})\textsubscript{4}.2H\textsubscript{2}O, which is obtained in solution by double decomposition of solutions of ammonium chloride and the silver salt. Upon evaporation it crystallises in colourless

\textsuperscript{1} Roessler, Zeitsch. anorg. Chem., 1897, 15, 405.
\textsuperscript{2} Rogers and Boyé, Amer. J. Sci., 1840, 38. 188; 1840, 39. 369; Weber, Pogg. Annalen, 1867, 131, 441.
\textsuperscript{3} Lang, J. prakt. Chem., 1861, [i], 83. 415.
\textsuperscript{4} Nilson, Bull. Soc. chim., 1877, [ii], 27, 242.
or faintly yellow rhombic prisms, which are stable in air but become anhydrous in vacuo. Upon heating, it decomposes with considerable violence, the mass becoming incandescent and swelling considerably, leaving a bulky mass of platinum sponge.

**Potassium Platinonitrite**\(^1, 2, 3\) K\(_2\)Pt(NO\(_2\))\(_4\), which may be prepared by adding potassium nitrite to a solution of potassium chlor-platinic in the requisite proportions. Upon cooling the salt separates out in colourless monoclinic crystals which are anhydrous. Upon recrystallisation from pure water, the dihydrate, K\(_2\)Pt(NO\(_2\))\(_4\).2H\(_2\)O, is obtained in rhombic crystals.

**Silver Platinonitrite**\(^1, 3\) Ag\(_2\)Pt(NO\(_2\))\(_4\), which is most conveniently prepared by addition of silver nitrate to a solution of the potassium salt. It crystallises in yellow monoclinic prisms, and is a useful starting-point for the preparation of other platinonitrites (see the ammonium salt, above).

In addition to the foregoing, the following platinonitrites have been described:

**Group A. Monovalent Metals**

- **Cæsiun**,\(^1\) Cs\(_2\)Pt(NO\(_2\))\(_4\)—Colourless prisms, stable in air, and but slightly soluble in cold water.
- **Lithium**,\(^1, 4\) Li\(_2\)Pt(NO\(_2\))\(_4\).3H\(_2\)O.—Brilliant prisms, inclined to be deliquescent, and losing the whole of their combined water at 100° C.
- **Rubidium**,\(^1\) Rb\(_2\)Pt(NO\(_2\))\(_4\)—Resembling the potassium salt. It can also be obtained in rhombic or hexagonal prisms combined with 2 molecules of water.
- **Sodium**,\(^2, 4\) Na\(_2\)Pt(NO\(_2\))\(_4\)—Flattened prisms, permanent in air, soluble in water.

**Group B. Divalent Metals**

- **Barium**,\(^1, 3\) BaPt(NO\(_2\))\(_4\).3H\(_2\)O.—Yellow prisms becoming anhydrous at 100° C.
- **Cadmium**,\(^1\) CdPt(NO\(_2\))\(_4\).3H\(_2\)O.—Oblique prisms, stable in air.
- **Calcium**,\(^1\) CaPt(NO\(_2\))\(_4\).5H\(_2\)O.—Yellow prisms. stable in air; completely dehydrated at 100° C.
- **Cobalt**,\(^1\) CoPt(NO\(_2\))\(_4\).8H\(_2\)O.—Red prisms, permanent in air, but decomposing at 100° C.
- **Copper**,\(^1\) CuPt(NO\(_2\))\(_4\).3H\(_2\)O.—Fine, green needles, soluble in water. A basic salt, 3CuPt(NO\(_2\))\(_4\).CuO.18H\(_2\)O, has also been obtained as yellow crystals.
- **Lead**,\(^1\) PbPt(NO\(_2\))\(_4\).3H\(_2\)O.—Stable, yellow prisms, which become anhydrous at 100° C.
- **Magnesium**,\(^1\) MgPt(NO\(_2\))\(_4\).5H\(_2\)O.—Elongated prisms, stable in air and at 100° C.
- **Manganese**,\(^1\) MnPt(NO\(_2\))\(_4\).9H\(_2\)O.—Prisms of pale rose colour which darken to brown in air and at 100° C. evolve nitrous fumes.
- **Nickel**,\(^1\) NiPt(NO\(_2\))\(_4\).8H\(_2\)O.—Stable green prisms, which decompose at 100° C.

\(^1\) Nilson, *Bull. Soc. chim.*, 1877, [iii], 27, 242.
\(^3\) Lang, *J. prakt. Chem.*, 1861, [i], 83, 415.
Strontium,\(^1,2\) SrPt\((\text{NO}_2)_4\).\(3\text{H}_2\text{O}\).—Yellow crystals, stable in air, but losing 2 molecules of water at 100 °C.

Zinc,\(^1\) ZnPt\((\text{NO}_2)_4\).\(8\text{H}_2\text{O}\).—Colourless prisms.

**Halogen Nitroplatinates**, M\(_2\)Pt\((\text{NO}_2)_4\).\(xX_x\).—Series of salts have been obtained in which the negative radicle contains both the nitro-group and halogens. The salts form interesting intermediaries between the tetranitro and tetrahalogen platinates already described. They are stable, and occur in well-defined crystalline forms. The best known salts are the di-iodo di-nitroplatinates of:

- **Aluminium**, Al\(_2\)[Pt\((\text{NO}_2)_2\).I\(_2\)].\(27\text{H}_2\text{O}\);
- **Ammonium**, (NH\(_4\))\(_2\)Pt\((\text{NO}_2)_2\).I\(_2\).\(2\text{H}_2\text{O}\);
- **Barium**, BaPt\((\text{NO}_2)_2\).I\(_2\).\(4\text{H}_2\text{O}\);
- **Calcium**, CaPt\((\text{NO}_2)_2\).I\(_2\).\(6\text{H}_2\text{O}\);
- **Cobalt**, CoPt\((\text{NO}_2)_2\).I\(_2\).\(8\text{H}_2\text{O}\);
- **Lithium**, Li\(_2\)Pt\((\text{NO}_2)_2\).I\(_2\).\(6\text{H}_2\text{O}\);
- **Magnesium**, MgPt\((\text{NO}_2)_2\).\(8\text{H}_2\text{O}\);
- **Nickel**, NiPt\((\text{NO}_2)_2\).I\(_2\).\(8\text{H}_2\text{O}\);
- **Potassium**, K\(_2\)Pt\((\text{NO}_2)_2\).I\(_2\).\(4\text{H}_2\text{O}\);
- **Radium**, RaPt\((\text{NO}_2)_2\).I\(_2\).\(8\text{H}_2\text{O}\);
- **Sodium**, Na\(_2\)Pt\((\text{NO}_2)_2\).I\(_2\).\(4\text{H}_2\text{O}\);
- **Strontium**, SrPt\((\text{NO}_2)_2\).I\(_2\).\(8\text{H}_2\text{O}\); and
- **Zinc**, ZnPt\((\text{NO}_2)_2\).I\(_2\).\(8\text{H}_2\text{O}\).

Iron yields two salts, namely:

- **Ferrous**, FePt\((\text{NO}_2)_3\).\(8\text{H}_2\text{O}\); and
- **Ferric**, Fe\(_3\)[Pt\((\text{NO}_2)_2\)].\(6\text{H}_2\text{O}\).

Lead and mercury yield basic salts, PbPt\((\text{NO}_2)_2\).I\(_2\).Pb(OH)\(_2\) and 2HgPt\((\text{NO}_2)_2\).Hg\(_2\text{O}\).\(9\text{H}_2\text{O}\).

Potassium mono- and dichlornitroplatinates, K\(_2\)Pt\((\text{NO}_2)_3\).Cl\(_2\).\(2\text{H}_2\text{O}\) and K\(_2\)Pt\((\text{NO}_2)_2\).Cl;

Potassium mono- and dibromnitroplatinates, K\(_2\)Pt\((\text{NO}_2)_3\).Br\(_2\).\(2\text{H}_2\text{O}\) and K\(_2\)Pt\((\text{NO}_2)_2\).Br\(_2\).\(9\text{H}_2\text{O}\) have also been prepared.\(^4\)

**Halogen Nitroplatinates**, M\(_2\)Pt\((\text{NO}_2)_6\).\(xX_x\).—These salts are intermediaries between the hexahalogen platinates and the hypothetical hexanitroplatinates. The best-known derivatives are\(^4\) the following potassium salts:

- **Dichlornitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_4\).Cl\(_2\);
- **Trichlornitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_3\).Cl\(_2\);
- **Pentachlornitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_5\).Cl\(_2\).\(\text{H}_2\text{O}\);
- **Dibromnitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_4\).Br;
- **Tri bromnitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_3\).Br;
- **Tetra bromnitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_2\).Br;
- **Tetra-iodonitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_2\).I;
- **Penta-iodonitroplatinate**, K\(_2\)Pt\((\text{NO}_2)_3\).I.

\(^1\) Nilson, *Bull. Soc. chim.*, 1877, [ii], 27, 242.
\(^3\) Nilson, *J. prakt. Chem.*, 1880, [ii], 21, 172; *Bull. Soc. chim.*, 1879, [ii], 31, 359.
Platinum and Phosphorus

Platinum appears to combine with phosphorus in several different proportions, but the state of our knowledge on this particular branch is not altogether satisfactory.

When platinum is heated to whiteness with yellow phosphorus in a Hessian crucible, fusion takes place and, when the excess of phosphorus has burned off, a brittle mass of empirical formula \( \text{Pt}_3\text{P}_5 \) is obtained on cooling.\(^1\) The same substance results on heating platinum in phosphorus vapour in a current of carbon dioxide. The temperature is raised to the point necessary to start the reaction, and the friable residue of \( \text{Pt}_3\text{P}_5 \) remains behind.

Presumably this is not a definite compound, but a mixture of monophosphide and diphosphide, namely, \( 2\text{PtP}_2 + \text{PtP} \).

**Platinum Subphosphide**, \( \text{Pt}_2\text{P} \), is obtained by submitting to prolonged roasting in a muffle the above-mentioned complex, \( \text{Pt}_3\text{P}_5 \), until constant weight is attained.\(^1\) It is a malleable substance, soluble in aqua regia.

**Platinum Monophosphide**, \( \text{PtP}_5 \), was presumably obtained by Pelletier in 1792\(^3\) as the result of heating platinum and phosphorus together until the metal had absorbed 18 per cent. of the phosphorus. The same phosphide is also obtained by boiling the complex \( \text{Pt}_3\text{P}_5 \), mentioned above, with aqua regia for many hours, whereby a residue of monophosphide is obtained, the diphosphide passing into solution.\(^1\)

**Platinum Diphosphide**, \( \text{PtP}_2 \), results when phosphorus vapour and carbon dioxide are passed over spongy platinum below red heat.\(^2\)

Davy\(^4\) obtained a product of empirical composition, \( \text{Pt}_3\text{P}_4 \), by heating platinum and phosphorus together *in vacuo*. It was insoluble in concentrated acids, and in this respect resembled the monophosphide. It may simply have been a mixture of \( 2\text{PtP} + \text{PtP}_5 \); on the other hand it may possibly indicate the existence of a definite compound of that formula.

Various compounds of platinum dichloride with phosphorus trichloride and with phosphorous acid have been prepared.\(^5\)

**Platinum and Arsenic**

An arsenide of platinum, \( \text{PtAs}_2 \), occurs in nature as the rare mineral *sperrylite*, and may be formed in the laboratory by heating platinum sponge with excess of arsenic, when the two elements unite with incandescence.

A few arsenites have been obtained.\(^6\)

---

PLATINUM AND ANTIMONY

With antimony platinum yields two simple compounds, namely, PtSb₂ and PtSb. A third compound, Pt₅Sb₂, appears also to be formed from alloys rich in platinum, when maintained several hours at 644° C.¹:

Platinum Di-antimonide, PtSb₂, is obtained in the form of grey, hexagonal (Christoffle) or octahedral (Roessler) crystals upon igniting a mixture of powdered antimony with platinum sponge.²

It is a hard substance which readily blackens upon heating.

PLATINUM CARBONYL DERIVATIVES

Carbonyl Chlorides.—By the alternate passage of chlorine and carbon monoxide over platinum sponge at 250° C., or simply by passing carbon monoxide over platinous chloride at the same temperature, a yellow sublimate is obtained consisting of a mixture of platinum dichloride dicarbonyl and sesquicarbonyl, namely, PtCl₂.2CO and 2PtCl₂.3CO respectively. The sublimate melts at about 150° C. to a red liquid, and upon heating to approximately 250° C. loses carbon monoxide, yielding the monocarbonyl, PtCl₂.CO.³

Monocarbonyl Platinum Dichloride, PtCl₂.CO, obtained by heating the di- and sesqui-carbonyls to 250° C., yields golden yellow crystals, melting at 195° C. to an orange-red liquid. The crystals are hygroscopic and are decomposed by water, the main reaction consisting in the deposition of platinum and liberation of carbon dioxide and hydrochloric acid; thus ³:

\[ \text{PtCl}_2\cdot\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{Pt} + 2\text{HCl}. \]

This reaction cannot, however, represent the whole of the changes taking place, since although on adding a drop of water to crystals of the monocarbonyl derivative a black deposit is obtained, the deposit is soluble both in concentrated hydrochloric acid and in concentrated nitric acid. It cannot, therefore, be merely platinum.

When heated to 300° C. the carbonyl decomposes, yielding platinum and phosgene, COCl₂.

Carbonyl platinum dichloride has a distinctly basic character. It dissolves in excess of hydrochloric acid to a lemon-yellow solution, due, perhaps, to the formation of a soluble hydrochloride, PtCl₂.CO.HCl. This solution is a powerful reducing agent, effecting the reduction of silver, gold, and mercury from their salts.⁴ The monocarbonyl unites with soluble metallic chlorides, such as those of the alkali metals, to yield yellow, crystalline double salts. These, however, are so readily soluble and so easily decomposed that their satisfactory isolation has proved difficult. With the chlorides of certain organic bases, however, well-defined compounds have been obtained.⁴

Sesquicarbonyl Platinum Dichloride, 2PtCl₂.3CO, results on heating the dicarbonyl to 250° C. in a current of carbon monoxide. It may

¹ Friedrich and Leroux, Metallurgie, 1909, 6, 1.
⁴ Mylius and Foerster, Ber., 1891, 24, 2424.
also be obtained by extracting the mixed carbonyl derivatives, resulting from passing carbon monoxide over platinous chloride, with hot carbon tetrachloride, in which it is more readily soluble, and evaporating the resulting solution. It crystallises in yellow needles, which melt at 180° C. At 250° C. it loses carbon monoxide, yielding the monocarbonyl derivative.

**Dicarbonyl Platinum Dichloride**, PtCl₂.2CO, is obtained by heating the monocarbonyl to 150° C. in a current of carbon monoxide. Upon sublimation in the gas it yields colourless needles melting at 142° C. to a yellow liquid. If raised to the melting-point in air, carbon monoxide is evolved. The residue solidifies and melts again at 190° C. A little above this temperature further decomposition sets in.

Dry hydrogen is without action in the cold, but at the melting-point the compound is at once reduced to the metal. If the hydrogen is burned the flame becomes luminous and, if made to impinge upon a cold porcelain surface, deposits a black film of platinum. Dry chlorine has no action until 80° or 90° C., when the compound fuses.¹

The dicarbonyl is decomposed by water, the chief reaction being as follows:²

$$\text{PtCl}_2 \cdot 2\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{CO} + \text{Pt} + 2\text{HCl}.$$  

**Diphosgene Platinum Dichloride**, PtCl₂.2COCl₂.—This compound was obtained by Pullinger as a non-volatile residue after passing streams of chlorine and carbon monoxide alternately over spongy platinum at 250° C. It is a yellow, crystalline solid, stable in dry air, but slightly deliquescent. It readily dissolves in water, but is recovered unaltered upon evaporation. When strongly heated it yields chlorine and phosgene together with a residue of metallic platinum.

**Carbonyl Platinum Dibromide**, PtBr₂, CO, was prepared by Pullinger¹ by passing a slow stream of dry carbon monoxide over platinum dibromide gradually heated to about 180° C.

It is also prepared by evaporating a solution of monocarbonyl platinum dichloride in hydrochloric acid on the water-bath in a current of hydrogen bromide. Upon recrystallisation from benzene it yields orange-red crystals, entirely free from platinum and platinous bromide.

The crystalline needles melt at 177-7° C.⁴ They dissolve in water to a red solution, which, however, almost instantly blackens, the black deposit, however, being soluble in hydrobromic acid.

When melted in a current of carbon dioxide it yields platinum dibromide.

With bromides of the alkali metals, etc., it yields a series of crystalline double salts.³

**Monocarbonyl Platinum Di-iodide**, PtI₂, CO, is obtained by adding dilute hydriodic acid to a solution of the carbonyl platinum dichloride in hydrochloric acid:

$$\text{PtCl}_2\text{CO} + 2\text{HI} = \text{PtI}_2\text{CO} + 2\text{HCl}.$$  

A brick-red, amorphous precipitate is obtained. This is purified by solution in and recovery from hydriodic acid and subsequent recrystallisation from benzene.

² Schützenberger, *loc. cit.*
³ Mylius and Foerster, *Ber.*, 1891, 24, 2424.
⁴ Pullinger, *loc. cit.* Mylius and Foerster give 181° to 182° C.
It may also be obtained by evaporating the mixed carbonyl derivatives, obtained by Schützenberger's method, with concentrated hydriodic acid, and recrystallising from benzene.

It yields red crystals, exhibiting a violet shimmer. They melt at 140° to 150° C., and decompose as the temperature is still further raised. They are decomposed by water rather slowly, whilst alkalies liberate metallic platinum.

With potassium iodide a double salt, PtI₂.CO.KI, is obtained as yellowish brown scales, which melt at 150° to 180° C. with decomposition. Other salts have been prepared, both with inorganic and with organic iodides.¹

**Carbonyl Platinum Monoxide**, PtO.CO, is presumably obtained when the hydrochloric acid solution of the carbonyl platinum dichloride is stirred into an acidified solution of ammonium acetate.¹ The liquid becomes violet in colour, and then deposits a bluish black, flocculent precipitate of what is presumably the carbonyl monoxide.

It is soluble in concentrated hydrochloric acid, yielding a yellow solution of the carbonyl platinum dichloride. With alkalies it reacts as follows:

\[
\text{PtO.CO} + 2\text{NaOH} = \text{Pt} + \text{Na₂CO₃} + \text{H₂O}.
\]

Stable *in vacuo* and in air, even on gently warming, it decomposes with slight explosion at 800° to 400° C., yielding metallic platinum and carbon dioxide.

**Carbonyl Platinum Monosulphide**, PtS.CO, is thrown down as a brown precipitate when hydrogen sulphide is passed into a solution of carbonyl platinum dichloride in hydrochloric acid ¹:

\[
\text{PtCl₂.CO} + \text{H₂S} = \text{PtS.CO} + 2\text{HCl}.
\]

It is an unstable substance, decomposing *in vacuo*, and burning with a slight explosion when heated to 300° or 400° C., yielding platinum, sulphur, and oxides of carbon and sulphur.

**Carbonyl Platinum Thiocyanate**, Pt(CNS)₂.CO.—A double salt of this substance with potassium thiocyanate, namely, Pt(CNS)₂.CO.KCNS, is obtained ¹ by adding a solution of potassium thiocyanate to one of carbonyl platinum dichloride in hydrochloric acid until the precipitate first formed is redissolved. On evaporation in the cold it crystallises in yellow needles, which decompose on warming with water.

**Platinum Thiocarbonate** is obtained in combination with 2 molecules of ammonia, PtCS₃(NH₃)₂·H₂O, by crystallisation from a mixture of potassium chlor-platinite, concentrated ammonia and carbon disulphide.² It yields red needles, insoluble in cold water, ammonium or sodium hydroxide. Exposed over sulphuric acid *in vacuo* it becomes anhydrous.

**PLATINUM AND CYANOGREN**

**Platinum Dicyanide, Platinous Cyanide**, Pt(CN)₂, appears to have been first obtained by Doebereiner ³ as the result of heating mercuric cyanogen.

¹ Mylius and Foerster, *loc. cit.*
platinocyanide, \( \text{HgPt(CN)}_4 \). It also results on treating the double potassium salt, \( K_2\text{Pt(CN)}_4 \) with chlorine, and by heating the ammonium salt, \( (\text{NH}_4)_2\text{Pt(CN)}_4 \), to 200° C. or 300° C. When mercuric cyanide is added to a solution of an alkali chlor-platinite, the liquid is decolorised, and platinous cyanide is deposited as a pale yellow precipitate. Prepared in these ways, platinous cyanide possesses a yellow colour. It is insoluble in alkalies and potassium cyanide, for which reason it cannot be used in preparing platinocyanides. When heated it burns, yielding metallic platinum.

A soluble form of platinous cyanide is obtained as a yellow precipitate by decomposing a solution of a platinocyanide with sulphuric acid. It dissolves easily in alkalies and in potassium cyanide solution, but is usually contaminated with small quantities of sulphate.

**Cyanoplatinous Acid**, \( \text{H}_4\text{Pt(CN)}_4 \) may be prepared by decomposition of its mercuric or cupric salt suspended in water by a current of hydrogen sulphide. On filtration and evaporation bluish black prisms are obtained, which deliquesce on exposure to moist air. The salt is easily soluble in water, alcohol and ether. At 100° C. it decomposes into platinous cyanide and hydrogen cyanide. Sulphuric acid converts it into platinous cyanide. The aqueous solution reacts strongly acid, decomposes carbonates, and has an acid taste. The alcoholic solution deposits a mirror of platinum on the containing vessel when heated.

**Cyanoplatininites or Platinocyanides**, \( \text{M}_2\text{Pt(CN)}_4 \)

Cyanoplatinous acid, like chlorplatinous acid, yields a series of well-defined salts of general formula \( \text{M}_2\text{Pt(CN)}_4 \). By analogy they should be termed cyanoplatininites, but it is more usual to refer to them as platinocyanides. The salts definitely contain the negative radicle \( \text{Pt(CN)}_4^- \), and are not, therefore, mere double salts of the type \( 2\text{MCN}\cdot\text{Pt(CN)}_2 \). They may be obtained by neutralising the free acid with their corresponding bases, but the method is not convenient. It is more usual to prepare them:

1. By double decomposition of the metallic sulphate with barium platinocyanide solution. Thus, for example, the magnesium salt was first prepared by Martius as follows:

\[
\text{MgSO}_4 + \text{BaPt(CN)}_4 = \text{MgPt(CN)}_4 + \text{BaSO}_4.
\]

2. By precipitation of the metallic platinocyanide, when insoluble in water, by double decomposition of a soluble salt of the metal with potassium platinocyanide solution. In this manner Martius obtained the copper salt:

\[
\text{CuSO}_4 + \text{K}_2\text{Pt(CN)}_4 = \text{CuPt(CN)}_4 + \text{K}_2\text{SO}_4.
\]

3. By warming platinum salt solutions with alkali or alkaline earth cyanides and allowing to crystallise. In this manner the potassium salt, the first platinocyanide to be obtained, namely, by Ittner, was prepared:

\[
6\text{KCN} + \text{PtCl}_4 = \text{K}_2\text{Pt(CN)}_4 + 4\text{KCl} + (\text{CN})_2.
\]

1. Knop, Annalen, 1842, 43, 111.
5. Doebereiner, loc. cit.
A more recent method consists in passing an alternating electric current through platinum electrodes immersed in aqueous solutions of the cyanides of the alkali or alkaline earth metals.¹

The platinocyanides are an interesting set of salts, remarkable, amongst other of their properties, for the tenacity with which they retain the electronegative metal (platinum) and disguise it to ordinary tests. Concentrated nitric or hydrochloric acid, alone or mixed, in the cold or on boiling, extracts no platinum from them. Even concentrated sulphuric acid only liberates platinum cyanide with difficulty.²

The platinocyanides yield very beautiful hydrates. The magnesium salt is an excellent example. It yields, upon slow evaporation of its solution, large regular prisms which appear deep red by transmitted light, but viewed by reflected light the sides of the prisms exhibit a brilliant beetle-green, and the extremities a deep blue or purple. This is the heptahydrate, MgPt(CN)₄·7H₂O. When gently warmed, even under water, the crystals become yellow, which colour characterises the dihydrated crystals deposited from solution at 45° to 50° C.

Isomerism.—In an interesting series of memoirs, Levy ³ has shown that certain hydrated platinocyanides, notably those of barium and calcium, exist in two modifications, having the same chemical composition and crystalline form, but exhibiting a remarkable difference in their optical characters, differing in colour and in the intensity of their fluorescence. The barium and calcium salts show this most distinctly, and the cerium salt only to a small extent. Other platinocyanides do not show this at all.

It is not easy to account for this isomerism according to the ordinary methods of representation of the structure of the platinocyanides. Since samples of anhydrous barium platinocyanide, derived from the isomeric tetrahydrates respectively, are equally fluorescent, it seems fairly certain that any scheme must take into consideration the combined water. Levy therefore suggests that the isomerism of the tetrahydrate may be accounted for by assuming that two molecules of water are attached to the barium and two to the platinocyanide radicles, since, in the case of the latter radicles, two alternative positions are possible, namely:

\[
\begin{align*}
\text{and} & \\
& 
\end{align*}
\]

It is conceivable that the β or asymmetrical form may be incapable of that movement under the stimulus of the incident radiations which,

in the case of the $\alpha$ or symmetrical isomeride, are able to excite fluorescence.

**Fluorescence.**—The majority of platinocyanides fluoresce under the stimulus of ultra-violet light\(^1\) or of radium radiations, although some salts show no sign of this property. Magnesium, erbium, yttrium, thallium and uranyl salts are cases in point.

It is certainly very remarkable that uranyl platinocyanide should fail to respond to the stimulus of ultra-violet light or to radium radiations. Both the uranyl and the platinocyanide groups can confer the property of fluorescence upon salts containing them, yet when they both occur in the same complex, there is no sign of fluorescence.

Fluorescence under the stimulus of radium emanations is usually exhibited in a marked degree by one hydrate of the platinocyanide whilst other hydrates either exhibit a feeble fluorescence or none at all. The anhydrous is frequently non-fluorescent also. For example, the heptahydrate of magnesium platinocyanide, MgPt(CN)\(_4\).7H\(_2\)O, is not fluorescent, although the pentahydrate, MgPt(CN)\(_4\).5H\(_2\)O, is markedly so. Again, the pentahydrate of calcium platinocyanide, CaPt(CN)\(_4\).5H\(_2\)O, exhibits intense fluorescence, whilst the anhydrous salt is only feebly fluorescent.

**Oxidation.**—In early literature\(^2\) it is stated that by the action of chlorine, bromine, iodine, lead peroxide or nitric acid upon potassium platinocyanide, a new product, potassium platinicyanide, K\(_2\)Pt(CN)\(_5\).3H\(_2\)O, is obtained. Similar statements may be found in some recent text-books, but are nevertheless quite incorrect.

When potassium platinocyanide in aqueous solution is acted upon by chlorine or bromine, a halogenated product of composition corresponding to the formula\(^3\) (in the case of bromine)

\[
\text{K}_2\text{Pt(CN)}_4\cdot\text{Br}_2\cdot6\text{K}_2\text{Pt(CN)}_4\cdot16\text{H}_2\text{O}
\]

is obtained, but no platinicyanide.

Oxidation of potassium platinocyanide with lead peroxide, acidulated with dilute sulphuric acid, yields a product containing the SO\(_4\) group,\(^4\) of formula \(x\text{K}_2\text{Pt(CN)}_4\cdot\text{K}_2\text{Pt(CN)}_4\cdot\text{SO}_4\), where \(x\) is probably 9; but again no platinicyanide is formed.

If, however, a solution of potassium platinocyanide is treated with hydrogen peroxide (20-volume solution) acidulated with dilute sulphuric acid, potassium platinicyanide, KPt(CN)\(_4\), is obtained, united with three molecules of platinocyanide, thus \(3\text{K}_2\text{Pt(CN)}_4\cdot\text{KPt(CN)}_4\cdot6\text{H}_2\text{O}\). Lithium platinocyanide is more readily oxidised in this manner, yielding \(2\text{Li}_2\text{Pt(CN)}_4\cdot\text{LiPt(CN)}_4\), and if the hydrogen peroxide is replaced by Merck's pure perhydrol, complete oxidation to lithium platinicyanide, LiPt(CN)\(_4\), is obtained.

The platinocyanides of the rare earth metals are crystalline salts which may be divided into two classes.\(^5\)

**Class I.** The cerium group, of general formula M\(_2\)Pt\(_3\)(CN)\(_{12}\).18H\(_2\)O.

---

5. See this Series, Vol. IV.
These are monoclinic, yellow in colour, with a blue reflex. Their densities and crystallographic constants are as follows:

\[
\begin{align*}
\text{Ce}_2\text{Pt}_3(\text{CN})_{12} \cdot 18\text{H}_2\text{O} & : a:b:c = 0.5806 : 1 : 0.5527 & \text{Density} = 107^\circ 33' & 2.657 \\
\text{La}_2\text{Pt}_3(\text{CN})_{12} \cdot 18\text{H}_2\text{O} & : - & - & 2.626 \\
\text{Di}_2\text{Pt}_3(\text{CN})_{12} \cdot 18\text{H}_2\text{O} & : a:b:c = 0.5806 : 1 : 0.5517 & \text{Density} = 107^\circ 29.5' & -
\end{align*}
\]

**CLASS II. The Yttrium Group**, of general formula M$_3$Pt$_3$(CN)$_{12}$ $\cdot 21$H$_2$O. These are rhombohedric, red in colour with a green reflex. Their densities and crystallographic constants are as follows:

\[
\begin{align*}
\text{Y}_3\text{Pt}_3(\text{CN})_{12} \cdot 21\text{H}_2\text{O} & : a:b:c = 0.8920 : 1 : 0.6157 & \text{Density} = 2.876 \\
\text{Gd}_3\text{Pt}_3(\text{CN})_{12} \cdot 21\text{H}_2\text{O} & : - & - & 2.563 \\
\text{Er }^3\text{Pt}_3(\text{CN})_{12} \cdot 21\text{H}_2\text{O} & : a:b:c = 0.8965 : 1 : 0.6194 & -
\end{align*}
\]

The more important platinocyanides are as follows:

**Aluminium Platinocyanide**, Al$_3$[Pt(CN)$_4$]$_3$, is prepared by addition of an aqueous solution of aluminium sulphate to one of barium platinocyanide. The barium sulphate is removed by filtration and the clear liquid allowed to crystallise. The salt separates out in blue, deliquescent laminae.

**Ammonium Platinocyanide**, (NH$_4$)$_2$[Pt(CN)$_4$] $\cdot 2$H$_2$O, is obtained when freshly prepared platinous cyanide is dissolved in ammonium cyanide solution. This method, however, does not give a perfectly pure product.

It may be prepared in a pure state by decomposing the barium derivative with ammonium sulphate solution. On concentrating the solution the salt crystallises out in citron-yellow prismatic needles which exhibit interesting trichroism, appearing greenish yellow, lavender-blue or rose colour according to position. Exposed over calcium chloride or sulphuric acid it loses one molecule of water, becoming white. At 100° to 150° C. it loses the whole of its water. The anhydrous salt may also be obtained by conducting ammonia gas over hydrogen platinocyanide at 100° C. At 300° C. it decomposes, yielding platinous cyanide. The monohydrated salt absorbs a second molecule of water on exposure to moist air.

**Barium Platinocyanide**, Ba[Pt(CN)$_4$] $\cdot 4$H$_2$O, is one of the most useful platinocyanides, inasmuch as it may be conveniently used in preparing other salts of hydrogen platinocyanide. Quadrat was the first to prepare it by boiling the copper derivative with barium hydroxide solution. Schafarik obtained it by decomposing barium carbonate with free platinocyanic acid. Martius boiled platinous cyanide with barium cyanide solution and obtained the salt, but recommended the following method as superior: Pulverised platinous chloride, PtCl$_2$, is added little by little to a boiling solution of barium cyanide in such a

---

1 For an account of the fluorescence of these salts see Levy, *loc. cit.*
4 Knop and Schnedermann, *Annalen*, 1847, 64, 300.
6 Quadrat, *Annalen*, 1847, 3, 64.
manner that no fresh chloride is added until the previous amount has completely dissolved and the solution become colourless. On crystallisation the salt is obtained in a very pure condition.

By electrolysis of a solution of barium cyanide between platinum electrodes, using an alternating current, a solution of barium platinumcyanide has been obtained \(^1\) which, upon concentration, crystallised out in yellow, slightly dichroic crystals, exhibiting a slight fluorescence under radium.

The salt may also be obtained by passing gaseous hydrogen cyanide into a pasty mixture of two parts of platinum dichloride and three of freshly precipitated barium carbonate with ten of water, maintained at nearly the boiling-point. The passage of gas is continued until effervescence ceases, and the solution is then boiled and filtered whilst hot. On cooling, the barium platinocyanide crystallises out in golden yellow, transparent crystals, exhibiting a purple sheen. The crystals frequently exhibit red and green colours on the edges, this effect being particularly noticeable when they are immersed in water.\(^2\) The crystals belong to the monoclinic system, the crystallographic elements \(^3\) being:

\[
a : b : c = 0.86928 : 1 : 0.47928. \quad \beta = 103° 54'.
\]

At 100°C. the salt loses two molecules of water, and becomes anhydrous at 140°–150°C, a yellowish blue powder remaining, which readily absorbs moisture on exposure to the air. The salt readily dissolves in hot water, but is insoluble in absolute alcohol.

Barium platinocyanide tetrahydrate can exist in two isomeric forms, which, however, are crystallographically identical. They differ in colour, density, and in fluorescence, as indicated in the following table \(^2\):

<table>
<thead>
<tr>
<th></th>
<th>(\alpha)-salt.</th>
<th>(\beta)-salt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Golden yellow</td>
<td>Apple-green</td>
</tr>
<tr>
<td>Density at 17°C</td>
<td>2.076</td>
<td>2.085</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Feeble</td>
<td>Intense</td>
</tr>
<tr>
<td>Stability</td>
<td>Less stable at the ordinary temperature</td>
<td>More stable at the ordinary temperature</td>
</tr>
<tr>
<td>Crystalline character</td>
<td>Same as (\beta)-salt</td>
<td>Same as (\alpha)-salt</td>
</tr>
</tbody>
</table>

When a solution of barium platinocyanide is allowed to crystallise after adding a trace of barium cyanide or barium hydroxide to it, crystals of the green \(\beta\)-salt are obtained. If, on the other hand, a trace of hydrogen cyanide, hydrogen chloride, tartaric or acetic acid, or cyanoplatinous acid is present instead, crystals of the yellow \(\alpha\)-salt are deposited.

The \(\beta\)-salt appears to be the more stable at ordinary temperatures.

The dihydrate and the anhydrous salt have also been prepared. The former is brick-red in colour and non-fluorescent. The latter is white and but feebly fluorescent.


Barium platinocyanide, after prolonged exposure to radiation from radium compounds, becomes brown or red and loses its fluorescent properties. The only way to completely restore the red crystals to their fluorescent state is by solution and recrystallisation, although gentle heating will partially restore them. This is well illustrated by the following table:

<table>
<thead>
<tr>
<th>(1) Fresh crystals</th>
<th>(2) Fresh crystals after exposure to β-rays from radium for eight hours</th>
<th>(3) Fresh crystals after exposure to β-rays from radium for forty-eight hours</th>
<th>(4) Red crystals (No. 3 above) after heating to 110°C in open tube</th>
<th>(5) Red crystals after heating to 120°C in sealed tube</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fluorescent Value. 100</td>
<td>Fluorescent Value. 8</td>
<td>Fluorescent Value. 8</td>
<td>Fluorescent Value. 27</td>
</tr>
</tbody>
</table>

Calcium Platinocyanide, CaPt(CN)₄.5H₂O, may be prepared in a similar manner to the barium salt. It crystallises in rhombic prisms, having the following crystallographic elements:

\[ a : b : c = 0.89956 : 1 : 0.34948 \]

Levy has shown that two isomorphic varieties of the pentahydrate exist, analogous to the two isomers of the tetrahydrate of barium platinocyanide. The α-salt may be described as golden yellow with green fluorescence on the pyramid faces, whilst the β-salt shows a green fluorescence on all faces, which is particularly intense on the tops of the crystals. The crystalline characters of the two isomerides are identical.

The α-salt is obtained by crystallisation from a solution containing a small quantity of acid, and the β-salt from one containing some hydroxyl or cyanide ions, precisely as in the case of the α and β barium platinocyanides.

Anhydrous calcium platinocyanide, CaPt(CN)₄, is white, and exhibits only a feeble fluorescence.

Calcium Ammonium and Calcium Potassium Platinocyanides have also been obtained.

Cerium Platinocyanide, Ce₃[Pt(CN)₄]₁₅.18H₂O, yields fluorescent crystals in two varieties, namely, yellow α-crystals and greenish yellow β-crystals, analogous to the two calcium isomerides.

Copper Platinocyanide, CuPt(CN)₄, is obtained as a gelatinous greenish blue precipitate on adding a solution of a copper salt to potassium platinocyanide. The precipitate is voluminous, shrinking on drying to an anhydrous greenish blue mass. When heated strongly it becomes dark green in colour, then evolves cyanogen vapours, and

---

2 The method used consisted in measuring the distance from the radium at which the salt, exposed on a tray of black paper, became distinctly visible in the dark. The salt was observed by means of a simple microscope fixed over the tray, and the intensity of the rays was taken to be inversely as the square of the distance between the radium and the salt.
3 Martius, opus cit.
finally yields a black mass containing platinum and copper oxide. The salt is not attacked by acids, but alkalis readily effect its decomposition. On account of this latter property it is a useful starting-point for the preparation of the platinocyanides of other metals.

**Hydrazine Platinocyanide**, ${\text{N}}_2{\text{H}}_4\cdot{\text{H}}_2{\text{Pt(CN)}}_4\cdot{\text{xH}}_2{\text{O}}$, may be obtained by mixing aqueous solutions of hydrazine sulphate and barium platinocyanide. On evaporation, the filtered solution deposits red crystals, which show blue and purple colours by reflected light. Owing to their instability when dried, analysis is difficult, but probably the red crystals are the **tetrahydrate**, ${\text{N}}_2{\text{H}}_4\cdot{\text{H}}_2{\text{Pt(CN)}}_4\cdot4{\text{H}}_2{\text{O}}$.

When air dried the crystals become light yellow and opaque, and correspond in composition to the **trihydrate**, ${\text{N}}_2{\text{H}}_4\cdot{\text{H}}_2{\text{Pt(CN)}}_4\cdot3{\text{H}}_2{\text{O}}$. When gently warmed they become white, the transformation occurring at about 28° C. Maintained at 100° C. for some time a dull, olive-green, anhydrous salt is obtained.

**Hydroxylamine Platinocyanide**, $(\text{NH}_2\text{OH})_2\cdot{\text{H}}_2{\text{Pt(CN)}}_4\cdot2{\text{H}}_2{\text{O}}$, has been prepared in a similar manner to the preceding salt. Upon crystallisation at the ordinary temperature, red crystals are deposited which are stable and admit of accurate analysis. When gently warmed they become yellow in colour, but return to their red hue on cooling. The change is probably due to partial dehydration.

**Indium Platinocyanide**, $\text{In}_2[\text{Pt(CN)}_4]_3\cdot2{\text{H}}_2{\text{O}}$, is prepared by boiling solutions of barium platinocyanide and indium sulphate together, filtering off the barium sulphate and allowing to crystallise out. It yields white, hygroscopic leaflets.

**Lead Platinocyanide**, $\text{PbPt(CN)}_4$, is readily prepared by mixing boiling saturated solutions of potassium platinocyanide and lead acetate. The solution remains clear, but on cooling the lead salt separates out as a yellowish white crystalline powder. It is anhydrous, and becomes yellow on warming in air, then white; whilst at higher temperatures cyanogen is liberated, the residue containing metallic lead and platinum.

**Lithium Platinocyanide**, $\text{Li}_2\text{Pt(CN)}_4\cdot5\text{H}_2\text{O}$, yields grass-green crystals, which undergo practically no change in colour when cooled in liquid air.

**Lithium Hydroxylamine Platinocyanide**, $\text{LiNH}_2\text{OHPt(CN)}_4\cdot3\text{H}_2\text{O}$, has been prepared. It yields purple, hygroscopic prisms.

**Magnesium Platinocyanide**, $\text{MgPt(CN)}_4\cdot7\text{H}_2\text{O}$, is conveniently prepared by decomposing the barium salt with magnesium sulphate solution. On filtering off the insoluble barium sulphate and allowing to evaporate, the salt crystallises out in blood- or carmine-red tetragonal crystals, possessing a metallic-green surface sheen. The parameters of the crystals are:

$$a : c = 1 : 1.06148.$$ 

There is no evidence that the salt can exist in two isomeric forms.
When maintained at 30° to 40°C., the *pentahydrate*, MgPt(CN)₂·5H₂O, is produced, which is yellowish green in colour. The same hydrate may be prepared by maintaining a hot saturated aqueous solution for some time at 45° to 50°C. until the salt separates out; as also by recrystallising the heptahydrated salt from alcoholic solution. The *dihydrate*, obtained at 100°C., is white, and the anhydrous salt, obtained by heating to 150° or 200°C., is yellow.¹ The following table² indicates the colour and fluorescent properties of anhydrous and hydrated salts:

<table>
<thead>
<tr>
<th>Colour.</th>
<th>Fluorescence.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgPt(CN)₂·7H₂O</td>
<td>Red with green reflection</td>
</tr>
<tr>
<td>MgPt(CN)₂·5H₂O</td>
<td>Yellowish green</td>
</tr>
<tr>
<td>MgPt(CN)₂·2H₂O</td>
<td>White</td>
</tr>
<tr>
<td>MgPt(CN)₂</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

The Platinocyanides of Mercury, HgPt(CN)₂, and Nickel, NiPt(CN)₂, have also been obtained.³

Potassium Platinocyanide or Gmelin's Salt, K₂Pt(CN)₂·3H₂O, was the first platinocyanide to be discovered, namely, by Ittner,⁴ who allowed mixed solutions of potassium cyanide and platinic chloride to crystallise. Ittner, however, does not appear to have understood the nature of the compound he had prepared. Gmelin,⁵ who discovered the ferricyanides, observed that by heating to redness a mixture of platinum sponge and potassium ferrocyanide, a compound results in which platinum replaces iron. Analysis of the product crystallised from water showed it to have the formula K₂Pt(CN)₂·3H₂O, when translated into modern symbols. Another method consists in mixing ammonium ⁶ chlor-platinite with water, adding caustic potash and raising to 100°C. Finally, saturated potassium cyanide solution is added. Ammonia is evolved, and potassium platinocyanide passes into solution:

$$2\text{KOH} + (\text{NH}_4)_2\text{PtCl}_4 + 4\text{KCN} = 2\text{NH}_3 + 4\text{KCl} + \text{K}_2\text{Pt(CN)}_2 + 2\text{H}_2\text{O}.$$  

After prolonged boiling to remove all the ammonia the solution is allowed to crystallise, when the salt separates out in long rhombic needles, density ⁷ 2·4548 at 16°C. Upon exposure to air the crystals effloresce, and at 120°C. lose three molecules of water, becoming pale golden yellow. The crushed crystals are sulphur-yellow in colour, but the crystalline faces exhibit a blue fluorescence. When dehydrated at ordinary temperatures the colour becomes reddish yellow. On heating, the salt becomes white, then yellow, and finally melts at 400–600°C. It is soluble in cold water, easily so in hot, as also in alcohol and ether. Dilute mineral acids do not affect it, but concentrated sulphuric acid effects the precipitation of platinous cyanide.

Wilm ⁸ drew attention to the fact that the properties of potassium platinocyanide vary somewhat according to the method of preparation. When white, fluorescent crystals of the salt are boiled with hydrogen

---

² Levy, *loc. cit.*
³ Martius, *loc. cit.*
⁴ See Berzelius, *Jahresber.*, 3, 45.
⁶ The potassium salt does not appear to work so well (Martius).
⁷ Clarke, *Amer. J. Sci.*, 1877, 14, 280. This figure, however, is uncertain owing to the presence of moisture.
⁸ Wilm, *Ber.*, 1888, 21, 1434.
peroxide (20 volume solution) the crystals remaining after evaporation are pale yellowish green in colour, but devoid of fluorescence. They constitute, in fact, an isomeride, into which the white, fluorescent salt has been converted, probably through the catalytic agency of some impurity in the peroxide. This catalytic theory is supported by the fact that by boiling the white, fluorescent crystals with pure perhydrol, no change takes place.\footnote{1}

Contrary to the statements of early investigators, oxidation of potassium platinocyanide with the halogens, nitric acid or lead peroxide, does not yield potassium platinocyanide. The halogens convert it into a dihalogenide, of general formula $K_2Pt(CN)_4\cdot X_2$. If, however, the solution of potassium platinocyanide is treated with hydrogen peroxide (20-volume solution) acidulated with dilute sulphuric acid, potassium platinocyanide, $KPt(CN)_4$, is obtained united with three molecules of platinocyanide, thus: $KPt(CN)_4\cdot 3K_2Pt(CN)_4\cdot 6H_2O$.

The crystallographic elements of the hydrated salt are \footnote{2}:

$$a:b:c = 0.8795 : 1 : 0.2736.$$  

**Potassium Barium Platinocyanide**, $BaK_2[Pt(CN)_4]_2\cdot Aq$, is obtained by crystallising mixed solutions of barium and potassium platinocyanides. In appearance it resembles the sodium potassium salt.\footnote{3}

**Potassium Lithium Platinocyanide**, $KLiPt(CN)_4\cdot 3H_2O$, has also been prepared \footnote{4} as yellowish green crystals.

**Radium Barium Platinocyanide.**—Since the majority of platinocyanides fluoresce under the influence of radiations from radioactive substances, the radium salt should be self-luminous. The radium barium salt was prepared \footnote{1} by dissolving radioactive barium chloride in water and boiling the solution with excess of silver platinocyanide. After filtering off insoluble silver salts the solution was allowed to crystallise in a desiccator.

The crystals deposited last were reddish in colour, and brightly luminous at first, but the intensity of their luminosity gradually diminished, and the reddish tint deepened in colour. No doubt this is attributable to alteration of the barium platinocyanide in the complex, since the free salt upon exposure to radium radiations undergoes some change, resulting in a weakening of the fluorescence as has already been pointed out (see p. 821).

The radium barium salt recovers its fluorescent properties upon recrystallisation, and the effect is enhanced by contact with its own saturated aqueous solution, probably because the water prevents the alteration referred to.

**Rubidium Platinocyanide**, \footnote{5} $Rb_2Pt(CN)_4\cdot 3H_2O$ (?) yields monoclinic crystals, the crystallographic elements being:

$$a:b:c = 0.9813 : 1 : 0.5325 \; ; \; \beta = 99^\circ 48.25^\prime.$$  

**Silver Platinocyanide**, $Ag_3Pt(CN)_4\cdot 6H_2O$, has also been prepared. It is white and does not blacken upon exposure to sunlight.

\footnote{1} Levy, Trans. Chem. Soc., 1908, 93, 1446.  
\footnote{2} Graflisch, Krystallographisch-optische Untersuchungen (Wien, 1888).  
\footnote{3} Martius, opus cit. See also Knop, Annalen, 1842, 43, 111.  
\footnote{4} Schröter. See Martius, opus cit., p. 45.  
Sodium Platinocyanide, Na₂Pt(CN)_4·3H₂O, was first prepared by Quadrat,¹ who decomposed the copper salt with sodium hydroxide. It also results on decomposing the barium salt with sodium sulphate.² Martius acted on the potassium salt in concentrated solution with hydrofluosilicic acid, and saturated the filtrate with sodium carbonate.

On concentration the salt separates out as long triclinic prisms³ closely resembling in properties the potassium salt. The crystallographic elements are:

\[ a:b:c = 0.5879 : 1 : 0.4757; \alpha = 87° 42' , \beta = 94° 56.75' , \gamma = 90° 59.5'. \]

The salt is soluble both in water and in alcohol. It loses its combined water at about 120° C.

Sodium Potassium Platinocyanide, NaKPt(CN)_4·3H₂O, results when the copper salt is decomposed with a mixed solution of sodium and potassium carbonates.⁴ It crystallises in beautiful orange-coloured monoclinic prisms, and closely resembles the barium potassium salt. Its crystallographic elements are⁵:

\[ a : b : c = 0.85694 : 1 : 0.47296; \beta = 95° 5'. \]

It differs from the potassium salt in that it does not effloresce in the air. At 120° C. it becomes anhydrous, turning pale yellow in colour, but developing a reddish brown hue upon exposure to sunlight.

Strontium Platinocyanide, SrPt(CN)_4·5H₂O, is most easily obtained by boiling the copper derivative with aqueous strontium hydroxide.⁴ The crystals form monoclinic tablets, milky white in colour, but exhibiting a delicate violet surface-tint and a green fluorescence. The crystallographic elements are⁶:

\[ a : b : c = 0.6850 : 1 : 0.4657; \beta = 94° 49'. \]

At 160° C. the salt becomes white and anhydrous. By crystallising mixed solutions of strontium and potassium platinocyanides the double salt Strontium Potassium Platinocyanide, SrK₂[Pt(CN)_4]₂·4H₂O, is obtained.

Uranil Platinocyanide, UO₂·Pt(CN)_4·4(or 5)H₂O, has been prepared⁶ by double decomposition of solutions of uranyl sulphate and barium platinocyanide. The green, filtered solution, upon evaporation at room temperature in a desiccator, deposits red crystals possessing a strong green metallic reflection.

If, however, the solution is concentrated on the water-bath, a yellow crystalline substance is obtained, which passes into the red-green form on cooling. Probably these changes are consequent upon variation in hydration.

The temperature of transformation of the red-green hydrate to the yellow salt is 30° C.

Zinc Platinocyanide, ZnPt(CN)_4, is obtained as an insoluble yellowish white product on treating potassium platinocyanide solution with

¹ Quadrat, Annalen, 1847, 3, 64.
⁴ Martius, opus cit.
⁵ Wilm, Ber., 1886, 17, 950.
zinc salts. Acids attack it with difficulty, but ammonia dissolves it readily.  

Halogen Cyanoplatinates, $M_2Pt(CN)_4X_2$

Dichlorcyanoplatinic Acid, $H_2Pt(CN)_4Cl_2$, has been obtained \(^2\) by decomposing the barium salt with dilute sulphuric acid and concentrating the filtered solution. It yields deliquescent crystals, which dissolve in water to an acid solution which decomposes carbonates.

The corresponding bromine derivative, $H_2Pt(CN)_4Br_2$, has been obtained, and several salts of these acids and of the iodo acid have also been prepared.  \(^3\)

Platinum Tricyanide, $Pt(CN)_3$, is obtained in a more or less pure condition as a yellow powder on heating cyanoplatinic acid to 120° C.  \(^4\)

Cyanoplatinates or Platinicyanides, $MPt(CN)_4$

Cyanoplatinic Acid, $HPt(CN)_4$—On adding hydrogen peroxide (20-volume solution) to a fairly concentrated solution of cyanoplatinous acid and evaporating over a water-bath, a white substance is first produced which, upon further evaporation, becomes pink, brown, and finally dull olive-green. Cyanoplatinic acid, $HPt(CN)_4 \cdot 2H_2O$, is left. On treating this last-named product with water it passes through the same colour changes, but in the reverse order, before dissolving, showing that the colours correspond to the formation of different hydrates:  \(^4\)

\[
2H_2Pt(CN)_4 + H_2O_2 = 2HPt(CN)_4 + 2H_2O.
\]

The aqueous solution of this acid liberates iodine from potassium iodide, the reaction being quantitative if sufficient time (several hours) is allowed. Thus:

\[
2HPt(CN)_4 + 2KI = 2KHPt(CN)_4 + I_2.
\]

Sulphur dioxide reduces the acid solution to cyanoplatinous acid. Heated to 120° C. the solid green acid is converted into a light yellow residue consisting mainly of platinum tricyanide, $Pt(CN)_3$.

Lithium Platinicyanide, $LiPt(CN)_4$, is obtained as the copper-coloured double salt, $LiPt(CN)_4 \cdot 2LiPt(CN)_4$, on warming hydrogen peroxide solution with lithium platinocyanide acidulated with sulphuric acid. If the platinocyanide solution is very concentrated or, better, if the hydrogen peroxide is replaced by perhydrol, pure lithium platinicyanide is obtained, free from admixed or combined platinocyanide.  \(^4\)

The anhydrous salt is white, and is readily obtained by gently heating one of its hydrates.

The monohydrate, \(^8\) $LiPt(CN)_4 \cdot H_2O$, is obtained by evaporation of an aqueous solution of the trihydrate and of sodium sulphate, and gently warming the residue. The sodium sulphatehydrates itself at the expense of the lithium salt, and the yellow monohydrated salt is

---

\(^4\) Levy, *opus cit.*  
obtained. The monohydrate is also produced on simply warming either the trihydrate or dihydrate.

The dihydrate, \( \text{LiPt(CN)}_4 \cdot 2\text{H}_2\text{O} \), may be prepared by gently warming the trihydrate, or by cooling it in liquid air. It is orange-red in colour, but readily dissolves in water to a colourless solution.

The trihydrate, \( \text{LiPt(CN)}_4 \cdot 3\text{H}_2\text{O} \), is obtained by evaporation of the aqueous solution at 40° to 50° C. to the crystallising point and suddenly cooling to 15° C. It yields needle-shaped crystals, which are colourless, but exhibit a slight lavender fluorescence.

Potassium Platinicyanide, \( \text{KPt(CN)}_4 \), is obtained, combined with three molecules of platinocyanide, namely, as \( 3\text{K}_2\text{Pt(CN)}_4 \cdot 6\text{H}_2\text{O} \), by adding hydrogen peroxide (20-volume solution) to a concentrated solution of potassium platinocyanide, acidulated with sulphuric acid. Bronze, needle-shaped crystals are deposited, displaying a strong metallic reflection. They are readily soluble in water, yielding a colourless solution from which no precipitate is obtained with barium chloride. The solution bleaches cochinine, and liberates iodine from potassium iodide. Thus:

\[ 3\text{K}_2\text{Pt(CN)}_4 \cdot \text{KPt(CN)}_4 + \text{KI} = 4\text{K}_2\text{Pt(CN)}_4 + \text{I} \]

Silver Platinicyanide, \( \text{AgPt(CN)}_4 \), is obtained as a light brown flocculent precipitate on adding silver nitrate solution to one of cyano-platinic acid. It dries to a dark buff powder which leaves a residue of metallic silver and platinum upon gentle ignition.

Sodium Platinicyanide, \( \text{NaPt(CN)}_4 \cdot 2\text{Na}_2\text{Pt(CN)}_4 \), has been obtained in a similar manner to the corresponding lithium salt.

**PLATINUM AND THIOCYANOGEN**

Platinum thiocyanates are not known, except in combination with the thiocyanates of certain other metals. Thiocyanoplatinic acid, \( \text{H}_2\text{Pt(CNS)}_4 \), and thiocyanoplattinic acid, \( \text{H}_2\text{Pt(CNS)}_6 \), are obtained in solution by decomposition of the corresponding barium salts with the calculated quantities of dilute sulphuric acid. The acids decompose, however, on concentration beyond a certain point.

**Thiocyanoplattinites, \( \text{M}_2\text{Pt(CNS)}_4 \)**

Potassium Thiocyanoplattinite, \( \text{K}_2\text{Pt(CNS)}_4 \), is obtained by crystallisation from mixed solutions of potassium chlorplatinite and thiocyanate. It yields red, hexagonal prisms which are readily soluble in warm water or alcohol, giving an orange-yellow solution.

The Ammonium salt, \( \text{(NH}_4)_2\text{Pt(CNS)}_4 \), has also been prepared by digesting ammonium chlor-platinite with a solution of an alkali thiocyanate until all has dissolved, and allowing to crystallise. It resembles the potassium salt.

The Silver salt, \( \text{Ag}_2\text{Pt(CNS)}_4 \), is known.

---

2. Levy, *opus cit.*


COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP

**THIOCYANOPLATINATES, M₂Pt(CNS)₆**

A few salts of thiocyanoplatinic acid have been prepared. They are analogous in constitution to the chlor- and thio-platinates, and are isomorphous with the corresponding selenocyanoplatinates.¹

**Ammonium Thiocyanoplatinate**, (NH₄)₂Pt(CNS)₆, is obtained on adding ammonium sulphate solution to one of potassium thiocyanoplatinate, and allowing to crystallise out.² It yields red, hexagonal prisms, which dissolve in water, but yield an unstable solution at the boiling-point. The parameters are ¹:

\[ a : c = 1 : 0.9340. \]

**Potassium Thiocyanoplatinate**, K₂Pt(CNS)₆, is formed when a warm solution of potassium thiocyanate is added to one of chlor-platimc acid or to a suspension of potassium chlor-platinate in water. It crystallises in red hexagonal prisms,³ the parameters being:

\[ a : c = 1 : 0.7829. \]

Density 2.342 at 18°C.⁴ The dihydrate, K₂Pt(CNS)₆·2H₂O, is known.⁵ It yields rhombic crystals ¹:

\[ a : b : c = 0.6224 : 1 : 0.9712. \]

The Silver,² Sodium, Barium,⁶ Strontium,⁶ and Lead salts have also been prepared. The dihydrate of the sodium salt is isomorphous with the corresponding potassium salt.¹

**PLATINUM AND SELENOCYANOGEN, M₂Pt(CNSe)₆**

A few salts of selenocyanoplatinic acid have been prepared. They are isomorphous with the corresponding thiocyanoplatinates.⁷

**Potassium Selenocyanoplatinate**, K₂Pt(CNSe)₆, is obtained by mixing solutions of potassium chlor-platinate and selenocyanate.⁸ It crystallises in hemimorphic rhombic crystals which appear red by transmitted light, and black by reflected light. The parameters are ⁷:

\[ a : b : c = 0.5989 : 1 : 0.9565. \]

Density 3.377 at 10.2°C.

The dihydrate, K₂Pt(CNSe)₆·2H₂O, yields trigonal scalenohedral crystals.⁷

**Ammonium Selenocyanoplatinate**, (NH₄)₂Pt(CNSe)₆, crystallises in the rhombic system ⁷:

\[ a : b : c = 0.6388 : 1 : 1.0444. \]

² Buckton, Annalen, 1854, 92, 280.
³ Buckton, loc. cit. Keferstein (Pogg. Annalen, 1856, 99, 275) described them incorrectly as regular octahedra.
⁴ Clarke, Jahresber., 1877, p. 43.
⁶ Gralich, Jahresber., 1858, p. 235.
⁸ Clarke and Dudley, Ber., 1878, 11, 1325.
PLATINUM AND SILICON

Several silicides of platinum have been stated at various times to exist, but it is doubtful if they are all separate chemical entities.\(^1\) The existence of the following silicides, however, seems reasonably well established.

**Diplatinum Silicide, Platinum Subsilicide**, \(\text{Pt}_2\text{Si}\), was apparently first obtained by Colson\(^2\) by prolonged heating of platinum surrounded by lampblack in a Hessian crucible. Lebeau\(^3\) prepared it by heating the monosilicide with tin and washing the product with potassium hydroxide, the subsilicide constituting the residue. Vigouroux\(^4\) prepared the subsilicide by heating the metal with 10 to 100 times its weight of silicon in an electric furnace to such a high temperature that excess of the silicon volatilised.

The product is a crystalline substance, hard and brittle, capable of being pounded to powder in a mortar. Density 13.8 at 18\(^\circ\) C. Heated in chlorine, silicon chloride is formed, leaving a residue of platinum.

**Platinum Monosilicide**, \(\text{PtSi}\), may be obtained by igniting a mixture of finely divided silicon and platinum sponge at a high temperature. On treating the melt with potassium hydroxide solution, excess of silicon is removed, leaving a residue of monosilicide.\(^5\) When recrystallised from fused silver silicide, the latter being removed by extraction with sodium hydroxide and nitric acid in succession, the monosilicide is obtained as prismatic crystals, melting at about 1100\(^\circ\) C., and of density 11.63 at 15\(^\circ\) C.

The usual mineral acids, including all the halogen acids, are without action upon it, but aqua regia effects its solution, and concentrated hydrochloric acid containing bromine also attacks it.

When heated with copper silicide, \(\text{Cu}_4\text{Si}\), it yields a double silicide, \(\text{PtCu}_2\text{Si}\),\(^4\) as a dense grey substance, completely soluble in aqua regia.

PLATINUM AND TIN

**Alloys** of platinum and tin have already been discussed (see p. 288).

**Platinum Stannate**, \(\text{Pt}_2\text{Sn}_6\text{O}_{12}\), and two **Platinum Thiostannates**, \(\text{Pt}_4\text{Sn}_8\) and \(\text{Pt}_3\text{Sn}_6\), have been described.\(^6\)

**Detection and Estimation of Platinum.**—See next Chapter.

---


\(^2\) Colson, *loc. cit.*

\(^3\) Lebeau and Novitzky, *Compt. rend.*, 1907, 145, 241.


CHAPTER X
DETECTION AND ESTIMATION OF THE PLATINUM METALS

Complete and trustworthy analyses of ores, etc., containing platinum metals are not easy to effect. They require on the part of the analyst considerable skill and expert knowledge of the eccentricities of the metals concerned. In the present chapter the more important reactions of the metals are outlined, together with the most usual methods of analysis.¹

DETECTION AND ESTIMATION OF RUTHENIUM

Detection.—Metallic Ruthenium is characterised by its ready solubility in a mixture of fused potassium hydroxide and nitrate, yielding a green mass of potassium ruthenate, \( K_2RuO_4 \). This dissolves in water to an orange-coloured solution which leaves a black stain upon the skin owing to the deposition of oxide or hydroxide. Nitric acid precipitates the hydroxide as a black mass from the solution.

Fused potassium hydrogen sulphate, which readily attacks rhodium, palladium and iridium, is without action upon ruthenium.

When heated with potassium chloride in a current of chlorine, ruthenium yields potassium chlor-ruthenate, \( K_2RuCl_6 \), which is soluble in water.

Metallic ruthenium is insoluble in the mineral acids, and is only slowly soluble in aqua regia.

Reactions of Salts of Ruthenium.—A delicate and characteristic reaction of ruthenium chloride consists in formation of an azure-blue tint (possibly due to the formation of dichloride) when hydrogen sulphide is passed through its solution in water.

Ammonium sulphide, on the other hand, causes a dark brown precipitate to separate out in like circumstances, which is soluble in excess only with difficulty.

Alkalies precipitate the black hydrated oxide, \( Ru_2O_3 \cdot 8H_2O \), insoluble in excess, but which is readily soluble in hydrochloric acid, yielding an orange solution containing the trichloride, \( RuCl_3 \).

With concentrated solutions of ruthenium salts, alkali chlorides effect the deposition of violet crystalline precipitates of the double chlorides. These are soluble in water only with difficulty, but are decomposed with boiling water, yielding black insoluble residues of oxychloride.

Ruthenium trichloride solution is reduced by metallic zinc to the dichloride, the colour changing from orange to azure-blue. In the presence of excess of zinc the reduction proceeds even further, metallic ruthenium being deposited as a black powder.

¹ As this is not a text-book of analysis the various operations are not discussed in experimental detail, but references are given so that the analyst desirous of attempting any of the methods may know where to look for full details.
### REACTIONS OF THE PLATINUM METALS

**IN COMPACT FORM**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling with aqua regia</td>
<td>Slowly dissolves</td>
<td>Insoluble save in certain alloys</td>
<td>Soluble (yielding OsO₄)</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Boiling with nitric acid</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Slowly soluble to palladous sulphate</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Boiling with sulphuric acid</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Slowly soluble to palladous sulphate</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td>Slightly attacked</td>
</tr>
<tr>
<td>Fusion with KHSO₄</td>
<td>No action</td>
<td>Forms soluble K₆Rh₂(SO₄)₆</td>
<td>Dissolved</td>
<td>—</td>
<td>Oxidised but not dissolved</td>
<td>Slightly attacked</td>
</tr>
<tr>
<td>Fusion with KOH and KNO₃</td>
<td>Green K₂RuO₄ sol. in water to orange soln.</td>
<td>Oxidised</td>
<td>Oxidised</td>
<td>Dissolved forming K₂OsO₄</td>
<td>Oxidised</td>
<td>Attacked</td>
</tr>
<tr>
<td>Treatment with iodine solution</td>
<td>—</td>
<td>—</td>
<td>Black stain</td>
<td>—</td>
<td>—</td>
<td>No action</td>
</tr>
</tbody>
</table>
REATIONS OF SALTS OF PLATINUM METALS

<table>
<thead>
<tr>
<th>COBALT, NICKEL, AND ELEMENTS OF PLATINUM GROUP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Colour</strong> 1</td>
</tr>
<tr>
<td>Ammonium sulphide</td>
</tr>
<tr>
<td>Ammonium hydroxide on warming</td>
</tr>
<tr>
<td>Saturated KCl solution 1 (1:1000)</td>
</tr>
<tr>
<td>KCNS, 1 per cent. solution</td>
</tr>
<tr>
<td>Dimethyl glyoxime</td>
</tr>
<tr>
<td>Ruthenium (RuCl₃)</td>
</tr>
<tr>
<td>Dark brown</td>
</tr>
<tr>
<td>Azure-blue colour on prolonged treatment</td>
</tr>
<tr>
<td>Dark brown ppte., Ru, difficult soluble in excess</td>
</tr>
<tr>
<td>Black ppte. of hydrated oxide insoluble in excess</td>
</tr>
<tr>
<td>Greenish colouring</td>
</tr>
<tr>
<td>Red cryst. ppte. of K₂RuCl₅</td>
</tr>
<tr>
<td>No change</td>
</tr>
<tr>
<td>Dark violet colour</td>
</tr>
<tr>
<td>Yellow ppte.</td>
</tr>
<tr>
<td>Ppte., Ru</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

1 With the platinum-metal salts in dilute solution. Based on the results of Mylius and Mazzucchelli, Zeitsch. anorg. Chem., 1914, 89, 1.
Detection of Ruthenium in Osmiridium.—Ruthenium may be detected in and separated from osmiridium by ignition in a current of oxygen at about 1080° C. Osmium tetroxide and ruthenium dioxide are volatilised, the latter being the first to condense.

Detection of Ruthenium in Platinum Alloys.—In order to detect the presence of ruthenium in platinum alloys, a portion of the alloy is fused with lead. The melt is extracted with nitric acid and the residue ignited in contact with air in order to volatilise the osmium. The mass may now contain platinum, iridium, rhodium and ruthenium, and is fused with potassium nitrate and hydroxide. The whole is dissolved in water, treated with excess of nitric acid and allowed to stand in a flask covered with filter-paper. In a few hours (12–24) the filter-paper darkens if ruthenium is present, in consequence of the evolution of vapour of its tetroxide. To confirm the presence of ruthenium, the paper is ignited and the ash fused with potassium nitrate and hydroxide. On extraction with water the orange colour of potassium ruthenate is obtained.1

Estimation.—Ruthenium may be estimated by precipitation with magnesium from solutions of its salts. The precipitate is washed with dilute sulphuric acid to remove excess of magnesium, dried, ignited in a current of hydrogen, cooled in carbon dioxide, and weighed as metal.

Ruthenium may be precipitated from solutions of its salts with hydrogen sulphide in the form of ruthenium sesquioxide. This is washed, dried, and ignited in a platinum boat in a current of oxygen to expel the sulphur, reduced in hydrogen and weighed as metal.

Ruthenium may be separated from all metals except osmium by distilling in alkaline solution in a current of chlorine at 70° C. The ruthenium distils over as tetroxide, and is collected in dilute hydrochloric acid. The liquid in the distilling-flask must be kept alkaline to prevent iridium chloride from distilling over with the ruthenium. The distillate is evaporated to dryness, and the residue ignited in hydrogen, cooled in carbon dioxide and weighed as metal.

Separation of Ruthenium from Osmium. See p. 388.

Separation of Ruthenium from the Platinum Metals. See Scheme I, p. 344.

DETECTION AND ESTIMATION OF RHODIUM

Detection.—Metallic Rhodium, when pure and compact, is insoluble in mineral acids, not excepting aqua regia, although it dissolves in the latter when alloyed with certain other elements such as lead, bismuth, copper and platinum, although not when alloyed with silver or gold. When fused with a mixture of potassium hydroxide and nitrate it is readily oxidised, whilst fusion with potassium hydrogen sulphate converts it into the soluble salt, potassium rhodium sulphate, RH₂(SO₄)₃·8K₂SO₄ or K₂Rh₂(SO₄)₆—a point of distinction between rhodium and ruthenium, since the latter metal is not affected by potassium hydrogen sulphate.

When heated with sodium chloride in a current of chlorine, the double chloride, sodium chlor-rhodite, Na₂RhCl₆·Aq., is formed, which dissolves in water, yielding a rose-red solution.

Reactions of Salts of Rhodium.—Ammonium sulphide effects the

precipitation of rhodium sesquisulphide from hot solutions of rhodium salts. In contradistinction to platinum and iridium sulphides, which are soluble in excess of ammonium sulphide, rhodium sulphide is insoluble in excess of this reagent.

Alkalies yield a yellowish brown precipitate of rhodium hydroxide, \( \text{Rh}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \), on boiling. This precipitate is soluble in excess of the reagent (contrast ruthenium).

Potassium hydroxide causes no precipitation from rhodium trichloride solution in the cold, but on adding alcohol a brown precipitate of hydroxide is obtained. This reaction is characteristic for rhodium.

Another noteworthy reaction consists in adding potassium nitrite to a solution of the trichloride, whereby an orange-yellow precipitate is obtained which is only slightly soluble in water and is but slightly decomposed by concentrated hydrochloric acid.

If the gases evolved by the action of hydrochloric acid upon potassium chlorate are passed into a solution of a rhodium salt rendered alkaline by addition of sodium hydroxide, the liquid becomes yellowish red, then red, and finally a slight green precipitate forms. This latter redissolves, yielding a blue solution containing sodium rhodate, \( \text{Na}_2\text{RhO}_4 \). This colour is destroyed by sodium peroxide or persulphate, and by sulphur dioxide.\(^1\)

Metallic rhodium is precipitated from solutions of its salts by addition of metallic zinc.

**Estimation.** Rhodium is conveniently estimated by precipitation with magnesium from solutions of its salts. The precipitate is washed with dilute sulphuric acid to remove excess of magnesium, dried, ignited in a current of hydrogen, cooled in carbon dioxide and weighed as metal.

Rhodium may also be estimated by reduction of its salts with hydrazine hydrate \(^2\) in hot alkaline solution, the concentration of the rhodium not being too great. The hydrosol first formed rapidly coagulates, yielding a metallic, glistening precipitate, gas being evolved the while in consequence of the catalytic action of the metal on the hydrazine. The precipitate is dried at 105° C., ignited in air, followed by hydrogen, and finally by carbon dioxide, in which gas it is cooled. The rhodium thus obtained is free from alkali.

**Separation of Rhodium from the Platinum Metals.** See Schemes I and II, pp. 344 and 345.

**DETECTION AND ESTIMATION OF FALLOIDUM**

**Detection.**—**Metallic palladium** is the most readily fused of the platinum metals (see Table, p. 5). When heated in air the surface becomes coated with oxides which tint it. The metal is soluble in aqua regia, sparingly soluble in nitric acid, but more readily soluble in the fuming acid, yielding palladous nitrate, from which a brown precipitate of basic salt may be obtained on dilution with water provided the acid is not present in too great an excess. A mixture of concentrated hydrochloric acid with chloric acid \(^3\) is recommended as a useful


solvent for palladium, inasmuch as it liberates free chlorine, which readily attacks the metal. Thus:

\[ 5\text{HCl} + \text{HClO}_3 = 3\text{Cl}_2 + 3\text{H}_2\text{O}. \]

Boiling, concentrated sulphuric or hydrochloric acid slowly dissolves the metal. Fused potassium hydrogen sulphate attacks palladium.

Reactions of Salts of Palladium.—Both hydrogen sulphide and ammonium sulphide effect the precipitation of black palladium monosulphide, \( \text{PdS} \), from solutions of its salts. The precipitate is insoluble in excess of ammonium sulphide, but dissolves on boiling with concentrated hydrochloric acid, and is soluble in aqua regia.

Caustic alkalis precipitate basic salts as yellowish brown deposits, soluble in excess. Water, alone, causes partial precipitation from acidulated solutions if acid is only present in very slight excess.

A characteristic reaction consists in the formation of a black precipitate of palladous iodide, \( \text{PdI}_2 \), on addition of alkali iodide. This tends to dissolve in excess of the alkali iodide, but is insoluble in hydrochloric acid.

Mercuric cyanide, \( \text{Hg(CN)}_2 \), precipitates palladous cyanide, \( \text{Pd(CN)}_2 \), from solution in the form of a yellowish white, gelatinous deposit, which is readily soluble in potassium cyanide, as also in ammonium hydroxide. This reaction is unique amongst the platinum metals, and serves as the basis of a useful method of separating and estimating palladium.

Addition of potassium chloride to a solution of palladous chloride causes the precipitation of the red potassium tetrachloropalladate, \( \text{K}_4\text{PdCl}_4 \), which dissolves in water to a red solution, but is insoluble in alcohol.

Palladium may be distinguished from copper, since ammonium thiocyanate yields no precipitate even after passage of sulphur dioxide.

Metallic zinc reduces palladous chloride solutions with deposition of finely divided metallic palladium.

Estimation.—Palladium may be estimated gravimetrically by addition of potassium chloride and alcohol to a concentrated solution of palladium chloride in hydrochloric acid. The brown precipitate of potassium chlor-palladite is collected, ignited, the potassium chloride washed out, and the residual palladium weighed as metal.

Palladium may be separated out from copper in this manner (see p. 344), but clearly cannot be separated from such metals as ruthenium, etc., which yield insoluble double chlorides with potassium chloride.

Palladium is frequently estimated by precipitation of palladous cyanide. To this end the chloride solution is almost completely neutralised with sodium carbonate and a solution of mercuric cyanide added. On gently warming until the odour of hydrogen cyanide has ceased, a whitish precipitate of palladous cyanide separates out. This is well washed, ignited, and the palladium weighed as metal.

This cyanide method is particularly useful because palladium is unique amongst the platinum metals in yielding a precipitate of cyanide on addition of mercuric cyanide; hence palladium admits of separation from its allies in this manner, and from most of the commoner metals too, notable exceptions being lead and copper.

Palladium may also be estimated by adding sodium hydroxide to a solution of the metal until the precipitate first formed has redissolved. Excess of alcohol is now added, and the whole kept on the water-bath
until the alcohol has disappeared. This is repeated, the liquid thoroughly boiled, and the precipitated palladium collected in a filter and ignited, first in air, then in hydrogen, and finally cooled in carbon dioxide.\(^1\)

Another method consists in precipitating the metal from its hot solution by addition of a hydrazine salt in acid solution.\(^2\) In this way palladium may be separated from aluminium and chromium, and indeed from nickel and cobalt if dilute solutions are employed. But the metal cannot be separated from mercury, lead, silver, platinum, copper or gold by this method, for although none of these metals are precipitated from solution by hydrogen salts alone, the presence of the palladium induces precipitation owing to the production of hydrogen.

When acetylene gas is passed through an acidified solution containing palladium, a brown precipitate is obtained which, upon ignition, yields palladium.\(^3\) In this way palladium may be quantitatively separated from copper.

**Separation of Palladium from Other Metals.**—Palladium may be separated from its allies also by addition of freshly precipitated silver iodide to a solution of their chlorides. Palladium chloride is the only one acted upon; it is converted into a black insoluble residue of iodide, the other metals remaining in solution. The washed precipitate is treated with potassium iodide solution or with aqua regia, whereby the palladium is dissolved out, and may be determined by ignition to the metallic condition.

Palladium may be conveniently estimated by precipitation with \(\alpha\)-nitroso \(\beta\)-naphthol in a similar manner to cobalt. The solution is acidified with hydrochloric and acetic acids, heated to boiling and precipitated with a hot, saturated solution of \(\alpha\)-nitroso \(\beta\)-naphthol in 50 per cent. acetic acid. A red coloration is produced, giving rise to a voluminous precipitate of the same colour, and having the composition \(\text{C}_{10}\text{H}_8\text{O}_2\text{N})_2\text{Pd}\). This is filtered off, washed, ignited in a current of hydrogen, and cooled in carbon dioxide, the palladium being weighed in the metallic condition.\(^4\) Since the other platinum metals are not precipitated in this manner, the foregoing affords a useful method of separation from them. The reaction is very sensitive, yielding a distinct precipitate, on standing, from a solution containing only 0·001 mg. of palladium ammonium chloride per c.c.\(^5\)

Palladium may also be precipitated with dimethyl glyoxime, and estimated in a similar manner.

**Palladium and Platinum** may be separated from each other by repeatedly evaporating their solution with hydrochloric acid, whereby the palladium is reduced to palladous chloride. On addition of ammonium chloride the platinum is precipitated as ammonium chloroplatinate, \((\text{NH}_4)_2\text{PtCl}_6\), leaving the palladium in solution,\(^6\) from which it may be obtained by the glyoxime method.

**Electrical Methods.**—Palladium may be estimated electrolytically by acidifying solutions of its salts with sulphuric acid, heating to 65° C.

\(^1\) Gutbier and Falco, Zeitsch. anal. Chem., 1909, 48, 555.
\(^2\) Jannasch and Bettges, Ber., 1904, 37, 2210. Jannasch and Rostosky, ibid., p. 2441.
\(^3\) Paal and Amberger, Ber., 1905, 38, 1388.
\(^4\) Erdmann and Makowska, Ber., 1904, 37, 2694.
\(^6\) W. Schmidt, Zeitsch. anorg. Chem., 1913, 80, 335.
DETECTION AND ESTIMATION OF THE PLATINUM METALS

and electrolysis at this temperature with a current of 0.25 ampere at 1.25 volts. The cathode may conveniently consist of a semicircular piece of platinum-gauze and the anode of a platinum-spiral. If tin is present, it remains in solution, a complete separation of the two metals being thereby effected. 

When a dilute solution of palladium is acidified with hydrochloric acid and reduced with carbon monoxide the electric conductivity increases considerably, the increase being proportional to the palladium and independent of the acidity. The increase in conductivity multiplied by $1.21 \times 10^{-4}$ gives the number of milligrams of palladium in 100 c.c. with a mean error of about 1 per cent.


DETECTION AND ESTIMATION OF OSMIUM

Detection.—Metallic osmium is characterised by its volatility at white heat without liquefaction, and by the production of volatile and excessively poisonous osmium tetroxide upon ignition of the finely divided metal in air or oxygen. The same vapour is evolved when any osmium compound is heated with concentrated nitric acid.

Fuming nitric acid and aqua regia each dissolve the metal unless the last named has previously been very strongly heated, in which case it is insoluble in all acids.

When heated with potassium chloride in a current of chlorine, osmium yields the tetrachloride, OsCl$_4$.

Reactions of Salts of Osmium.—All compounds of osmium are reduced to the metal upon ignition in hydrogen. Hydrogen sulphide in acid solution effects the precipitation of brownish black osmium monosulphide, OsS, which is insoluble in ammonium sulphide.

Alkalies precipitate hydrated osmium dioxide, Os(OH)$_4$, as a brownish red mass, whilst grey anhydrous osmium dioxide is obtained on fusing potassium hexachlor osmate, K$_3$OsCl$_6$, with sodium carbonate.

Osmium tetroxide dissolves in water, yielding a neutral solution possessed of oxidising activity. For example, it oxidises ferrous sulphate to the ferric condition, being itself reduced to the dioxide and thrown out of solution in the black hydrated condition, Os(OH)$_4$ or OsO$_2$.2H$_2$O.

Sulphurous acid or sulphur dioxide added to the solution yields a series of colour-changes ranging from yellow through green to blue, the last named being the colour of osmium sulphite, which then separates out. Metallic zinc effects the reduction and precipitation of metallic osmium from solution as a black powder, readily distinguished and separated from the allied platinum metals in that it is soluble in hydrogen peroxide.

A delicate colour-reaction for osmium consists in warming a solution containing the metal, in the form of its tetroxide or as chlorosmate, with thiocarbamide in excess, together with a few drops of hydrochloric acid. The presence of osmium is indicated by the development of a

---

2 Donau, Monatsh., 1906, 27, 59.

VOL. IX: 1
deep red or rose colour, due to the formation of a complex of composition represented by the formula \([\text{Os}_6\text{CS(NH}_2)_2]\text{Cl}_3\cdot\text{IL}_2\text{O}\). The colour is sufficiently intense to enable the detection of one part of osmium in 100,000.\(^1\)

**Estimation.** Osmium may be estimated with considerable accuracy by decomposing an alkali osmate with a slight excess of dilute sulphuric acid, in the presence of a little alcohol to prevent reoxidation. After ten to twelve hours a bluish black deposit containing the whole of the osmium is obtained. This is filtered and reduced in hydrogen. Fremy's method of precipitating osmium as sulphide does not yield accurate results.\(^3\)

When present in various compounds or alloys, osmium is conveniently estimated by ignition in a current of oxygen, collection in alcoholic alkali of the volatile tetroxide, and reduction with formaldehyde. The reduction product first forms a colloid, but is gradually precipitated and converted in metallic osmium by reduction in hydrogen at 230° to 250° C.\(^3\) Or the alcoholic solution may be treated with ammonium chloride and the precipitated osmyl diammine chloride reduced to metal in hydrogen.

**Volumetric** methods have been suggested, notably that of Klobbie,\(^4\) which consists in treating a solution of osmium tetroxide in dilute sulphuric acid with potassium iodide and titrating the liberated iodine with sodium thiosulphate. One molecule of osmium tetroxide liberates four atoms of iodine. The solution becomes dark green, but no further reduction takes place even after several days.

**Separation of Osmium** from ruthenium, rhodium, iridium and platinum may be effected by addition of zinc or magnesium to the solution containing these metals, whereby they are all precipitated as a black deposit.

Addition of hydrogen peroxide effects the solution of the osmium, the other metals remaining unaffected. The osmium may then be estimated by any of the foregoing methods.

**Separation of Osmium from Ruthenium.**—The metals are precipitated together from solution as sulphides by passage of hydrogen sulphide through the acidified solution. The precipitate is dried and ignited in a platinum-boat in a current of oxygen; the ruthenium remains behind as the dioxide, \(\text{RuO}_2\), in which condition it is weighed, or, if desired, it may be reduced to metal by ignition in hydrogen, cooled in carbon dioxide, and weighed as metal. The osmium volatilises as tetroxide, \(\text{OsO}_4\), and is collected in 12 per cent. sodium hydroxide solution admixed with 2 per cent. of alcohol.

Addition of aluminium-strip effects the precipitation of metallic osmium, which is collected in an asbestos-packed tube and dried at dull red heat in hydrogen, cooled in carbon dioxide, and weighed.

**Separation of Osmium from Osmiridium.** See p. 340.

**Separation of Osmium from the Platinum Metals.** See Schemes I and II, pp. 344 and 345.

---

\(^1\) Tschugaev, *Compt. rend.*, 1918, 167, 235.


\(^3\) Paal and Amberger, *Ber.*, 1907, 40, 1378.

DETECTION AND ESTIMATION OF IRIDIUM

Detection.—Metallic Iridium, like rhodium, is insoluble in all acids, save that in a very finely divided condition it is slowly attacked by aqua regia. Fusion with potassium hydrogen sulphate oxidises the metal but does not effect its solution (contrast ruthenium and rhodium). When fused with a mixture of potassium nitrate and hydroxide an insoluble residue containing the sesquioxide, \( \text{Ir}_2\text{O}_3 \), with alkali is obtained.

Reactions of Salts of Iridium.—Hydrogen sulphide in excess causes the precipitation of dark brown iridium sesquisulphide, \( \text{Ir}_2\text{S}_3 \). If the iridium is present in solution in the tetravalent condition, as for example in the form of alkali chlor-iridates, \( \text{M}_2\text{IrCl}_4 \) or \( 2\text{MCl} \cdot \text{IrCl}_4 \), the dark solution is first decolorised and a yellowish white precipitate of sulphur forms in consequence of the reduction of the iridium salt to the trivalent condition, namely, as \( \text{IrCl}_3 \). When this has been accomplished the brown sesquisulphide is obtained.

Ammonium sulphide yields the same precipitate, soluble in excess.

Alkali hydroxides in excess give the solution a green tint and precipitate a little double chloride. On heating the solution a red tint develops, changing to a deep azure blue in consequence of the precipitation of the hydrated dioxide, \( \text{Ir(OH)}_4 \). This serves to distinguish iridium from platinum.

Potassium chloride and ammonium chloride precipitate from concentrated solutions their respective chlor-iridates, \( \text{K}_2\text{IrCl}_4 \) and \( (\text{NH}_4)_2\text{IrCl}_6 \), as brownish red deposits.

Addition of reducing agents such as ferrous sulphate or stannous chloride to solutions of the alkali chlor-iridates reduces them to double salts of iridium trichloride, namely, \( 8\text{MCl} \cdot \text{IrCl}_3 \) or \( \text{M}_2\text{IrCl}_6 \), known generally as chlor-iridites. The solution is simultaneously decolorised, and the salts crystallise out on cooling.

Metallic zinc reduces iridium salts to the metal, which is deposited as a black powder from solution.

Alcohol reduces iridic salts to the corresponding iridous compounds.

Estimation.—Iridium is conveniently estimated by igniting ammonium chlor-iridate in hydrogen, and weighing as metal. To this end, solutions containing iridium salts are evaporated with aqua regia, ammonium chloride added, and the chlor-iridate, \( (\text{NH}_4)_2\text{IrCl}_6 \), collected and ignited.

Separation of Iridium and Platinum.—Quennessen recommends dissolving the alloy in a mixture of one part by volume of nitric acid (density 1.82) with two parts of hydrochloric acid (density 1.18) and evaporating to dryness. The residue is heated to 120° C., dissolved in water and precipitated with magnesium. The deposited metals are ignited at dull redness to render the iridium insoluble, treated first with dilute sulphuric acid to extract the magnesium, and then with diluted aqua regia to extract the platinum, leaving the iridium as an insoluble residue.

Another method consists in melting the alloy of platinum and iridium with ten times its weight of lead in a carbon crucible, and

repeatedly digesting the button thus obtained with hot, dilute nitric acid. The insoluble residue is then digested with aqua regia, diluted with water, and the residue of iridium washed, ignited and weighed.

The iridium content of commercial platinum may be rapidly determined colorimetrically as follows: The metal is dissolved in aqua regia, evaporated to dryness and taken up with concentrated hydrochloric acid. The color of the solution thus obtained is compared with that of a standard solution of platinum and iridium in the same solvent.

Analysis of Osmiridium. Osmiridium, in a finely divided condition, is intimately mixed with four times its weight of sodium peroxide and added to fused sodium hydroxide in a nickel crucible. On treating the product with water and washing the residue with sodium hypo-chlorite solution, a solution is obtained which holds all the osmium and ruthenium as alkali osmate and ruthenate respectively, and some of the iridium as iridate.

The solution is distilled with chlorine at 70°C, the vaporised tetroxides of osmium and ruthenium being collected in dilute hydrochloric acid, and the metals may be separated and estimated as explained on page 338. The liquid in the distilling-flask must be kept alkaline to prevent iridium also passing over as chloride with the osmium and ruthenium. The residual solution containing the iridium is acidified with hydrochloric acid, the residue from the fusion dissolved with it, and the iridium estimated as indicated above.

DETECTION AND ESTIMATION OF PLATINUM

Detection. Metallic platinum is insoluble in the individual mineral acids, but readily dissolves in aqua regia, yielding platinic chloride, PtCl₄. A mixture of chloric acid with excess of hydrochloric acid has been recommended as a useful solvent for platinum, the mechanism of the reaction depending, as in aqua regia, upon the liberation of free chlorine. Thus:

\[ 5\text{HCl} + \text{HClO}_3 = 3\text{Cl}_2 + 3\text{H}_2\text{O}. \]

When present in certain alloys, platinum is dissolved by nitric acid. When fused with caustic alkalies or potassium nitrate, platinum is oxidised.

Platinum sponge dissolves in boiling potassium cyanide solution.

Reactions of Platinum Salts. Hydrogen sulphide slowly causes the deposition of a dark brown precipitate of platinic sulphide, PtS₂, which is soluble in aqua regia, but insoluble in nitric acid and in hydrochloric acid separately.

Ammonium sulphide precipitates the disulphide from solution; it is soluble in excess of the yellow ammonium sulphide, yielding the thio salt, (NH₄)₂PtS₃.

Ammonium chloride produces a yellow precipitate of ammonium chlor-platinate, (NH₄)₄PtCl₆, which is slightly soluble in water, but insoluble in alcohol.

---

1 Mylius and Mazzucchelli, Zeitsch. anorg. Chem., 1914, 89, 1.
2 Leidi6 and Quennessen, Compt. rend., 1903, 136, 1399.
Platinum salts are readily reduced to the metal by ferrous sulphate and stannous chloride solutions.

Solutions of platinic chloride yield a blood-red colour with stannous chloride unless in very dilute solution, when the colour is a golden brown. On shaking with ether the colour is extracted.¹ This reaction is useful since it is not given by iridium or palladium, nor yet by iron or gold. Filter-paper, however, gives coloration after treatment with aqua regia, so that in testing for platinum any filter-paper or organic matter of a humic nature should be destroyed by fusion with pyrosulphate prior to extraction with aqua regia.²

Oxalic acid, on the other hand, does not reduce platinic chloride although it reduces gold solutions, depositing metallic gold. This often affords a convenient method of separating the two metals.

Metallic platinum is precipitated from solutions of its salts by metallic zinc.

**Estimation.**—Platinum may be estimated by acidulating the solution of its salts with hydrochloric acid and passing hydrogen sulphide through. The platinum is precipitated as disulphide, ignited and weighed as metal. The precipitated sulphide is difficult to filter. Gaze recommends addition of mercuric chloride to the solution, whereby the platinum sulphide comes down with mercuric sulphide in a manageable form. The latter disappears by volatilisation during ignition.³

An obvious disadvantage lies in the fact that the bulk of the precipitate is increased, and of course the mercuric vapours evolved upon ignition are poisonous. For these reasons magnesium chloride has been recommended, since the presence of this salt in solution assists precipitation of the platinum sulphide, which is obtained in a pure state upon washing with acidulated water.⁴

Platinum is conveniently estimated by almost neutralising an acid solution of its salts with ammonia, and concentrating until crystallisation sets in. Sufficient water is now added to just dissolve the crystals, and excess of saturated ammonium chloride solution. After thorough mixing an excess of alcohol is added, and the whole allowed to stand for twenty-four hours, after which the precipitate of ammonium chloroplatinate, \((NH_4)\text{PtCl}_4\), is collected on asbestos in a crucible, washed with 80 per cent. alcohol, and either weighed as such after drying, or ignited in a current of hydrogen and weighed as metallic platinum.

**Volumetric Methods.**—A useful volumetric method consists in adding platinic chloride or an alkali chlor-platinate to a cold concentrated solution of potassium iodide.⁵ The iodine liberated, according to the equation

\[
\text{PtCl}_4 + 4\text{KI} = \text{PtI}_2 + 4\text{KCl} + \text{I}_2
\]

is estimated by titration with sodium thiosulphate in the usual way, with starch as indicator.

**Colorometric Methods** have been recommended.⁶

The purity of a sample of platinum may be checked by determining

⁵ Peterson, Zeitsch. anorg. Chem., 1899, 19, 59; Grampe, Ber., 1874, 7, 1721.
the thermo-electric force of a couple consisting of the sample and a known standard platinum alloy.\(^1\)

*A Microchemical Method* of estimating traces of platinum in gold and silver is described by van Breukeleven.\(^2\)

**COMPLETE ANALYSIS OF THE PLATINUM METALS**

**A. Qualitative Analysis.**—Several methods may be employed for the qualitative determination of the platinum metals. The procedure is necessarily varied somewhat according to the nature and number of other metals present. These frequently comprise gold, mercury, arsenic, antimony, and tin.

**Scheme I**

One method consists in passing hydrogen sulphide into the hot acidified solution of the chlorides until no further precipitation occurs. After washing, the precipitate is warmed with yellow ammonium sulphide, and the whole filtered.

The insoluble residue, which may contain Ru, Rh, Pd and Os, is fused with KO\(_2\)H + KClO\(_3\), extracted with water and filtered.

The residue is ignited in hydrogen and extracted with HNO\(_3\). The insoluble residue may contain Rh and Pd. Aqua regia is added.

Any rhodium remains as an insoluble residue. The solution is evaporated, the residue dissolved in water, almost neutralised with Na\(_2\)CO\(_3\). A white precipitate on adding Hg(CN)\(_2\) indicates palladium.

A black precipitate of oxide indicates ruthenium.

Distil the filtrate with HNO\(_3\). Volatile OsO\(_4\) indicates osmium.

Black residue is iridium.

Platinum, if present, is obtained as sponge by igniting the residue.

The solution may contain Pt, Ir and Au, contaminated with As, Sb and Sn. HCl is added and the precipitated sulphides fused with Na\(_2\)CO\(_3\)+Na\(_2\)NO\(_3\). Extraction with water removes As as soluble arsenate. The residue is reduced with Zn + HCl. Boiling with HCl dissolves out the Sn. Again boiling with HNO\(_3\) and tartaric acid removes Sb. The residue is heated to dull redness to render iridium insoluble. Diluted aqua regia is added.

The solution may contain Pt and Au. Take to dryness on water-bath with excess of NH\(_4\)Cl. Treat with alcohol in which AuCl\(_3\) is soluble; filter.

Any gold in the filtrate is precipitated by addition of ferrous sulphate solution.

---


DETECTION AND ESTIMATION OF THE PLATINUM METALS

Scheme II

Mylius and Dietz\(^1\) recommend boiling the solution of the metallic chlorides with dilute nitric acid, and collecting the distillate in sodium hydroxide solution, which becomes yellow if osmium is present, since the latter passes over with the steam as volatile OsO\(_4\). The residual liquid is shaken with ether to extract any gold chloride, and then boiled with ammonium acetate and formic acid for several hours in a flask fitted with a vertical condenser. The metals are reduced to a black precipitate which is washed, dried and heated to redness in hydrogen to expel any mercury. The residue after treatment with hydrochloric acid is mixed with sodium chloride and ignited in chlorine. On dissolving the resulting product in water, and adding ammonium chloride, Pt, Ir and Ru are precipitated, whilst Pd and Rh remain in solution. This separation is not quantitative, but suffices for qualitative analysis.

1. Mylius and Dietz, Ber., 1898, 31, 3191.
2. This reduces the ruthenium and iridium to trichlorides.
B. Quantitative Analysis.—A complete quantitative analysis of the platinum metals is a complicated process, and several useful schemes have been suggested. Two only are given here:

**Scheme I**

This is based on that recommended by Mellor.\(^1\) It is not elaborate, but yields quite good results.

1. **Treat with aqua regia.** Fuse any insoluble residue with \(\text{Na}_2\text{O}_2\), and dissolve in HCl. Mix the two solutions. Following metals may be present: Ru, Rh, Pd, Os, Ir, Pt, as well as Au, Cu, Fe, Ni.\(^2\)

2. Distil in chlorine

3. Volatile portion is collected in NaOH solution. Contains **Ruthenium, Osmium.** Separate as per page 338.

4. **Solution contains Platinum,** with merest traces of palladium which may be neglected. Estimate as per p. 341.

5. **Residual solution is boiled to expel chlorine, \(\text{NH}_4\text{Cl}\) and two-thirds its volume of alcohol added.**

6. **Precipitate contains Pt, Ir, some Rh, and traces of Pd. Ignite and extract with aqua regia.**

7. **Filtrate contains Rh, Pd, with Cu, Fe, Ni. Nearly neutralise with \(\text{NH}_4\text{OH}\). Add \(\text{H}_2\text{S}\).**

8. **Solution contains Iridium with, perhaps, a trace of rhodium. Estimate as per p. 339.**

9. **Residue contains oxidised Iridium with, perhaps, a trace of rhodium. Estimate as per p. 339.**

10. **Residue contains oxidised Rhodium. Estimate as per p. 334.**


2. From the nickel crucible used.
Scheme II

The following scheme of Wunder and Thürringer is based on Deville and Debray’s classical method already detailed in preceding pages.

The ore containing Fe, Cu, Au, Pt, Ir, Rh, and Pd is decomposed with aqua regia after any particles of Au have been mechanically separated.

The residue of sand, osmiridium, etc., is fused with borax and metallic silver. The resulting silver button is heated with nitric acid and the insoluble residue of Osmiridium is weighed and analysed (p. 340).

The precipitate consists of the double ammonium chlorides of platinum and iridium. Ignite and weigh the metals. Treat with aqua regia to dissolve out the platinum.

The residue is Iridium. The solution contains Cu, Rh, and traces of Ir and Pt. Treat with dilute nitric acid (1:1).

The precipitate is metallic Gold, which is completely thrown down in this way.

The solution is boiled with dimethyl glyoxime.

The precipitate consists of palladium dimethyl glyoxime. Ignite to yield metallic Palladium.

Reduce the solution with zinc and hydrochloric acid.

The solution contains Iron.

The precipitate contains Cu, Rh, and traces of Ir and Pt. Treat with dilute nitric acid extracted with conc. HCl.

The solution is evaporated with HCl to remove HNO₃ and the Copper estimated.

The precipitate contains Rhodium sulphate. Addition of zinc precipitates Rhodium.

The solution contains Rhodium.

The residue consists of Ir and Pt, which may be separated as indicated above.

The gold thrown out of solution by the dimethyl glyoxime is usually contaminated with traces of platinum. The whole is dissolved in aqua regia and the platinum precipitated in the usual way with ammonium chloride. The gold is then precipitated in the metallic condition with ammonium oxalate.

NOTE 1. The platinum obtained from the ignited mixture of platinum and iridium by extraction with aqua regia, and subsequent precipitation as the double ammonium chloride, and ignition usually contains a little iridium. The process should therefore be repeated.

NOTE 2. The gold thrown out of solution by the dimethyl glyoxime is usually contaminated with traces of platinum. The whole is dissolved in aqua regia and the platinum precipitated in the usual way with ammonium chloride. The gold is then precipitated in the metallic condition with ammonium oxalate.

NAME INDEX

ABOULBNO, 95
Ackworth, 29
Adams, 111
Adhicary, 93, 94
Adie, 60, 61
Allaire, 74, 134
Allmavst, 49, 116
Altmayer, 92
Alvarez, 68, 218, 334
Amborg, 190, 337
Amberger, 156, 195, 210, 220, 238, 184–188, 270, 336, 338
Anderson, 298
Andrews, 107, 135, 275
Antony, 141, 142, 148, 149, 237, 239, 250, 306
Archibald, 241, 274, 276, 277, 293, 294, 299–301
Arena, 196, 239
Arvedson, 119
Armit, 67, 132
Armstrong, 29
Arthur, 135
Atack, 135
Athanasesco, 55, 123
Aubel, 263
BAAR, 109
Babo, von, 40
Baeyer, 69
Baikow, 91
Bailey, 118, 189
Baker, 121
Balard, 298
Bannister, 339
Barker, 339
Barbiori, 15, 38, 111, 125
Barclay, 34, 35, 100, 102
Barns, 159
Barr, 263
Barrett, 27
Bartels, 95
Barth, 37
Baschieri, 11
Basset, 40, 41, 269
Baubigny, 98, 117, 119
Bauer, 193, 281
Baumhauer, 320, 321, 324, 325
Baxter, 28, 29, 32, 33, 42, 266
Bayley, 47, 51, 118
Bedmar, 179
Bequerei, 26, 51
Bedford, 95
Beetz, 47, 48, 67
Beilby, 59, 125, 266, 321
Belucci, 12, 51, 52, 117, 118, 120, 132, 196, 206, 275, 283, 296, 297, 300, 302, 304, 305
Belynski, 37
Benesh, 295
Benner, 290
Bennington, 129, 130
Benrath, 43
Beresteyn, van, 94
Berger, 115, 264
Berglund, 52, 121
Bergmann, 20, 26, 80
Berneck, von, 269, 271
Bernoulli, 132
Berry, 179, 187, 192
Bersch, 39, 40
Berthelot, 42, 112, 131, 317
Bertiner, 132
Berthollet, 267
Berti-Ceroni, 184, 195, 198, 199
Bertrand, 67
Berzelius, 30, 44, 73, 110, 158, 159, 162, 166, 167, 189, 201–203, 206, 206, 211, 212, 214, 216, 221, 222, 226, 228, 229, 231, 239, 242, 250–252, 276, 285, 303, 304, 323
Bfet, 42
Betzges, 195, 336
Bettinck, 47
Bettel, 65
Beylund, 63
Bianchi, 103, 134
Bichowsky, 11
Biggs, 179
Billows, 328
Birkbaum, 247, 248, 250, 251, 295, 307
Blackadder, 157
Blomstrand, 326
Blondel, 290, 297, 304, 305, 308
Blumer, 298
Bodewig, 196
Böcking, 258
Boedeker, 64, 291, 300
Böhm, 38, 110
Böseken, 194, 268
Boetger, 99
Bätter, 238, 273, 286, 287, 306
Boettgeringer, 52, 121
Bogdan, 57
Bohart, 125, 126, 133
Boisbaudran, 26, 122, 249
Bolschakoff, 44, 112
Bombardini, 40
Bonsdorff, 197–199, 295, 300

347
<table>
<thead>
<tr>
<th>Name</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borck</td>
<td>11</td>
</tr>
<tr>
<td>Bormann</td>
<td>91, 131</td>
</tr>
<tr>
<td>Bornemann</td>
<td>86, 119, 120, 214, 215, 220, 338</td>
</tr>
<tr>
<td>Borsard</td>
<td>95</td>
</tr>
<tr>
<td>Botone</td>
<td>26, 27, 90</td>
</tr>
<tr>
<td>Bouchonnet</td>
<td>252</td>
</tr>
<tr>
<td>Bourbon</td>
<td>109</td>
</tr>
<tr>
<td>Bourgeois</td>
<td>73, 133, 284</td>
</tr>
<tr>
<td>Boussingault</td>
<td>212, 241, 256, 267</td>
</tr>
<tr>
<td>Boutzoureano</td>
<td>57, 124</td>
</tr>
<tr>
<td>Boyé</td>
<td>309</td>
</tr>
<tr>
<td>Brandt</td>
<td>20</td>
</tr>
<tr>
<td>Braun</td>
<td>70</td>
</tr>
<tr>
<td>Brearley</td>
<td>135</td>
</tr>
<tr>
<td>Bredig</td>
<td>157, 184-186, 269-272</td>
</tr>
<tr>
<td>Breed</td>
<td>112, 135, 152, 159, 242, 263, 264, 280, 342</td>
</tr>
<tr>
<td>Breitauer</td>
<td>317, 320</td>
</tr>
<tr>
<td>Broniewski</td>
<td>155</td>
</tr>
<tr>
<td>Brossa</td>
<td>239</td>
</tr>
<tr>
<td>Browne</td>
<td>85</td>
</tr>
<tr>
<td>Brunck</td>
<td>36, 107, 135, 183, 280</td>
</tr>
<tr>
<td>Brunjes</td>
<td>117</td>
</tr>
<tr>
<td>Bruyn</td>
<td>54, 122</td>
</tr>
<tr>
<td>Buquet</td>
<td>131</td>
</tr>
<tr>
<td>Burali</td>
<td>141, 149, 150, 231</td>
</tr>
<tr>
<td>Brochet</td>
<td>317, 320</td>
</tr>
<tr>
<td>Brodský</td>
<td>155</td>
</tr>
<tr>
<td>Brouwer</td>
<td>125</td>
</tr>
<tr>
<td>Burgstatter</td>
<td>47</td>
</tr>
<tr>
<td>Cailletet</td>
<td>137</td>
</tr>
<tr>
<td>Calcagni</td>
<td>56</td>
</tr>
<tr>
<td>Calvert</td>
<td>268</td>
</tr>
<tr>
<td>Calzolari</td>
<td>33, 111</td>
</tr>
<tr>
<td>Campbell</td>
<td>112, 135, 152, 183, 250</td>
</tr>
<tr>
<td>Camoll</td>
<td>184</td>
</tr>
<tr>
<td>Carmichael</td>
<td>233</td>
</tr>
<tr>
<td>Carmelley</td>
<td>27, 50</td>
</tr>
<tr>
<td>Carnot</td>
<td>70, 75</td>
</tr>
<tr>
<td>Carpenter</td>
<td>92</td>
</tr>
<tr>
<td>Castoro</td>
<td>42, 138, 184, 210, 269</td>
</tr>
<tr>
<td>Cerdan</td>
<td>256</td>
</tr>
<tr>
<td>Cesari</td>
<td>108, 196</td>
</tr>
<tr>
<td>Chaibrié</td>
<td>252</td>
</tr>
<tr>
<td>Chapin</td>
<td>75</td>
</tr>
<tr>
<td>Charlton</td>
<td>80, 99</td>
</tr>
<tr>
<td>Charpy</td>
<td>40, 81</td>
</tr>
<tr>
<td>Chassevant, Le</td>
<td>40, 42, 111</td>
</tr>
<tr>
<td>Chatelier, Le</td>
<td>157, 262</td>
</tr>
<tr>
<td>Chauvenet</td>
<td>109</td>
</tr>
<tr>
<td>Chéneveau</td>
<td>263</td>
</tr>
<tr>
<td>Chesneau</td>
<td>52</td>
</tr>
<tr>
<td>Chlopín</td>
<td>115, 119</td>
</tr>
<tr>
<td>Chouriguine</td>
<td>280</td>
</tr>
<tr>
<td>Chretien</td>
<td>125</td>
</tr>
<tr>
<td>Christiansen</td>
<td>57, 73, 300</td>
</tr>
<tr>
<td>Christoffe</td>
<td>318</td>
</tr>
<tr>
<td>Clarke</td>
<td>78, 110, 114, 115, 126, 129, 132, 150, 194, 254, 287, 312, 323, 328</td>
</tr>
<tr>
<td>Claus</td>
<td>75, 136, 137, 139, 140-149, 151, 159-167, 172, 214, 217, 219-221, 229-234, 242-244, 248-251, 254, 327</td>
</tr>
<tr>
<td>Clavari</td>
<td>117, 118</td>
</tr>
<tr>
<td>Clementi</td>
<td>301</td>
</tr>
<tr>
<td>Cleve</td>
<td>295</td>
</tr>
<tr>
<td>Cloud</td>
<td>155</td>
</tr>
<tr>
<td>Cochín</td>
<td>312</td>
</tr>
<tr>
<td>Coehn</td>
<td>50</td>
</tr>
<tr>
<td>Coffin</td>
<td>33</td>
</tr>
<tr>
<td>Cohen</td>
<td>7, 71, 138, 157, 239, 275</td>
</tr>
<tr>
<td>Cohn</td>
<td>132</td>
</tr>
<tr>
<td>Coleman</td>
<td>82</td>
</tr>
<tr>
<td>Collardeau</td>
<td>137</td>
</tr>
<tr>
<td>Collie</td>
<td>177</td>
</tr>
<tr>
<td>Collie</td>
<td>255</td>
</tr>
<tr>
<td>Colson</td>
<td>267, 329</td>
</tr>
<tr>
<td>Combes</td>
<td>107</td>
</tr>
<tr>
<td>Conneéck</td>
<td>39</td>
</tr>
<tr>
<td>Conquet</td>
<td>265</td>
</tr>
<tr>
<td>Corroy</td>
<td>265</td>
</tr>
<tr>
<td>Cooke</td>
<td>1, 274, 291</td>
</tr>
<tr>
<td>Cooper</td>
<td>34, 98, 121, 122, 273</td>
</tr>
<tr>
<td>Copaux</td>
<td>22, 23, 27, 28, 56, 57, 75, 90-92</td>
</tr>
<tr>
<td>Coquillon</td>
<td>183</td>
</tr>
<tr>
<td>Corelli</td>
<td>132</td>
</tr>
<tr>
<td>Corenwindörfer</td>
<td>268</td>
</tr>
<tr>
<td>Costachesous</td>
<td>38, 110</td>
</tr>
<tr>
<td>Cowap</td>
<td>66, 161</td>
</tr>
<tr>
<td>Croft</td>
<td>198</td>
</tr>
<tr>
<td>Crookes</td>
<td>155, 157, 176, 240, 264, 287, 293, 294</td>
</tr>
<tr>
<td>Crossley</td>
<td>94</td>
</tr>
<tr>
<td>Cunningham</td>
<td>60, 61</td>
</tr>
<tr>
<td>Cuntze</td>
<td>71</td>
</tr>
<tr>
<td>Curtius</td>
<td>59, 125</td>
</tr>
<tr>
<td>Curtmann</td>
<td>7</td>
</tr>
<tr>
<td>Cushman</td>
<td>29, 97, 111, 112, 116</td>
</tr>
<tr>
<td>Czudnowicz</td>
<td>321</td>
</tr>
<tr>
<td>Daha</td>
<td>208, 212, 235, 258</td>
</tr>
<tr>
<td>Darapsky</td>
<td>125</td>
</tr>
<tr>
<td>Daubree</td>
<td>256</td>
</tr>
<tr>
<td>Davis</td>
<td>26, 81</td>
</tr>
<tr>
<td>Davison</td>
<td>295, 257</td>
</tr>
<tr>
<td>Davy</td>
<td>273, 306, 312</td>
</tr>
<tr>
<td>Day</td>
<td>91, 176, 263</td>
</tr>
<tr>
<td>Debus</td>
<td>268</td>
</tr>
<tr>
<td>Dede</td>
<td>75</td>
</tr>
<tr>
<td>Delépine</td>
<td>243-246, 252, 265, 266, 274, 280, 307</td>
</tr>
<tr>
<td>Demarcey</td>
<td>166</td>
</tr>
<tr>
<td>Denham</td>
<td>41</td>
</tr>
<tr>
<td>Desborough</td>
<td>281, 284</td>
</tr>
<tr>
<td>Descamps</td>
<td>68, 129</td>
</tr>
<tr>
<td>Descotille</td>
<td>260</td>
</tr>
<tr>
<td>Dewar</td>
<td>120, 131, 159, 194</td>
</tr>
<tr>
<td>Dickson</td>
<td>257</td>
</tr>
<tr>
<td>Name</td>
<td>Pages</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Didier</td>
<td>129</td>
</tr>
<tr>
<td>Dietz</td>
<td>289, 343</td>
</tr>
<tr>
<td>Dinklage</td>
<td>232</td>
</tr>
<tr>
<td>Ditschener</td>
<td>324</td>
</tr>
<tr>
<td>Ditte</td>
<td>46, 62, 74, 111, 114, 126, 130, 133, 134</td>
</tr>
<tr>
<td>Dittenberger</td>
<td>289</td>
</tr>
<tr>
<td>Dittmar</td>
<td>93, 158, 275, 291</td>
</tr>
<tr>
<td>Dittrich</td>
<td>77</td>
</tr>
<tr>
<td>Dobroserdoff</td>
<td>44, 121</td>
</tr>
<tr>
<td>Doebereiner</td>
<td>1, 209, 237, 273, 303, 304, 315, 316</td>
</tr>
<tr>
<td>Doernicke</td>
<td>280, 281, 284</td>
</tr>
<tr>
<td>Dominici</td>
<td>51</td>
</tr>
<tr>
<td>Donath</td>
<td>209, 216, 237, 238, 240, 245, 247, 249, 250, 254</td>
</tr>
<tr>
<td>Donau</td>
<td>196, 337</td>
</tr>
<tr>
<td>Donnan</td>
<td>40</td>
</tr>
<tr>
<td>Dougherty</td>
<td>135</td>
</tr>
<tr>
<td>Dourdie</td>
<td>108</td>
</tr>
<tr>
<td>Driek</td>
<td>28</td>
</tr>
<tr>
<td>Drouin</td>
<td>196</td>
</tr>
<tr>
<td>Ducelliez</td>
<td>36, 37, 42, 65, 66, 112</td>
</tr>
<tr>
<td>Ducru</td>
<td>65, 130</td>
</tr>
<tr>
<td>Dudley</td>
<td>328</td>
</tr>
<tr>
<td>Dufan</td>
<td>51, 117</td>
</tr>
<tr>
<td>Dufet</td>
<td>148, 150-152, 205, 234, 244, 245</td>
</tr>
<tr>
<td>Duffour</td>
<td>162, 244</td>
</tr>
<tr>
<td>Dufos</td>
<td>21</td>
</tr>
<tr>
<td>Dulong</td>
<td>210, 263</td>
</tr>
<tr>
<td>Dumas</td>
<td>1, 31, 98</td>
</tr>
<tr>
<td>Dunbar</td>
<td>104</td>
</tr>
<tr>
<td>Durrant</td>
<td>51, 68</td>
</tr>
<tr>
<td>Edison</td>
<td>100</td>
</tr>
<tr>
<td>Eggert</td>
<td>272</td>
</tr>
<tr>
<td>Eichler</td>
<td>220</td>
</tr>
<tr>
<td>Eliaischke</td>
<td>58</td>
</tr>
<tr>
<td>Elser</td>
<td>263</td>
</tr>
<tr>
<td>Elten</td>
<td>52, 121</td>
</tr>
<tr>
<td>Emich</td>
<td>240</td>
</tr>
<tr>
<td>Emslander</td>
<td>337</td>
</tr>
<tr>
<td>Engel</td>
<td>39, 40, 290</td>
</tr>
<tr>
<td>Engelsmann</td>
<td>102</td>
</tr>
<tr>
<td>Engle</td>
<td>76</td>
</tr>
<tr>
<td>Engler</td>
<td>69</td>
</tr>
<tr>
<td>Erdmann</td>
<td>43, 59-61, 95, 97, 111, 113, 122, 126, 127, 134, 336</td>
</tr>
<tr>
<td>Erhart</td>
<td>222</td>
</tr>
<tr>
<td>Espil</td>
<td>115</td>
</tr>
<tr>
<td>Etard</td>
<td>39, 40, 43, 44, 53, 54, 112, 113, 122</td>
</tr>
<tr>
<td>Ewen</td>
<td>264</td>
</tr>
<tr>
<td>Ezer</td>
<td>28, 92, 138, 155, 176, 200, 238, 263</td>
</tr>
<tr>
<td>Fabaro</td>
<td>263</td>
</tr>
<tr>
<td>Fahrcnwald</td>
<td>192, 278</td>
</tr>
<tr>
<td>Falco</td>
<td>336</td>
</tr>
<tr>
<td>Faraday</td>
<td>212, 241, 263</td>
</tr>
<tr>
<td>Farmer</td>
<td>272</td>
</tr>
<tr>
<td>Fehling</td>
<td>206</td>
</tr>
<tr>
<td>Felgate</td>
<td>93</td>
</tr>
<tr>
<td>Fellenberg</td>
<td>52, 120, 159, 167, 203, 242, 250</td>
</tr>
<tr>
<td>Fellner</td>
<td>337</td>
</tr>
<tr>
<td>Ferrand</td>
<td>129</td>
</tr>
<tr>
<td>Féry</td>
<td>263</td>
</tr>
<tr>
<td>Field</td>
<td>67</td>
</tr>
<tr>
<td>Pink</td>
<td>205</td>
</tr>
<tr>
<td>Fischer</td>
<td>60, 126, 172, 201, 205, 222</td>
</tr>
<tr>
<td>Fischl</td>
<td>95</td>
</tr>
<tr>
<td>Fitzau</td>
<td>155, 176, 238, 262</td>
</tr>
<tr>
<td>Flescher</td>
<td>76</td>
</tr>
<tr>
<td>Fleitmann</td>
<td>80</td>
</tr>
<tr>
<td>Fleming</td>
<td>159, 194</td>
</tr>
<tr>
<td>Flight</td>
<td>99</td>
</tr>
<tr>
<td>Foerster</td>
<td>102, 268, 313-315</td>
</tr>
<tr>
<td>Fontaine</td>
<td>312</td>
</tr>
<tr>
<td>Fonsee-Daco</td>
<td>57, 123</td>
</tr>
<tr>
<td>Forste</td>
<td>111</td>
</tr>
<tr>
<td>Fordos</td>
<td>120</td>
</tr>
<tr>
<td>Fortini</td>
<td>134</td>
</tr>
<tr>
<td>Fortner</td>
<td>134-186</td>
</tr>
<tr>
<td>Foster</td>
<td>93, 268</td>
</tr>
<tr>
<td>Fouqué</td>
<td>119</td>
</tr>
<tr>
<td>Friedenhanen</td>
<td>93</td>
</tr>
<tr>
<td>Freese</td>
<td>65, 125</td>
</tr>
<tr>
<td>Frey</td>
<td>44, 50, 53, 63, 169, 211, 220, 221, 228, 231</td>
</tr>
<tr>
<td>Freylich</td>
<td>204</td>
</tr>
<tr>
<td>Fresenius</td>
<td>26</td>
</tr>
<tr>
<td>Frey</td>
<td>303, 304</td>
</tr>
<tr>
<td>Erich</td>
<td>167, 241</td>
</tr>
<tr>
<td>Friedel</td>
<td>163</td>
</tr>
<tr>
<td>Friedholm</td>
<td>58</td>
</tr>
<tr>
<td>Friedrich</td>
<td>52, 65, 129-131, 313</td>
</tr>
<tr>
<td>Friend</td>
<td>270-272</td>
</tr>
<tr>
<td>Frilley</td>
<td>133</td>
</tr>
<tr>
<td>Fritzsche</td>
<td>231, 232</td>
</tr>
<tr>
<td>Fullerton</td>
<td>46</td>
</tr>
<tr>
<td>Funk</td>
<td>62, 63, 126, 127</td>
</tr>
<tr>
<td>Garnier</td>
<td>79</td>
</tr>
<tr>
<td>Gauhe</td>
<td>75</td>
</tr>
<tr>
<td>Gauthier</td>
<td>108, 109</td>
</tr>
<tr>
<td>Gaze</td>
<td>341</td>
</tr>
<tr>
<td>Gebhardt</td>
<td>191</td>
</tr>
<tr>
<td>Gisbel</td>
<td>192, 267</td>
</tr>
<tr>
<td>Geisenheimer</td>
<td>247-250, 254</td>
</tr>
<tr>
<td>Geittner</td>
<td>51, 121, 306</td>
</tr>
<tr>
<td>Gélys</td>
<td>120</td>
</tr>
<tr>
<td>Gendel</td>
<td>47</td>
</tr>
<tr>
<td>Gentz</td>
<td>49, 115</td>
</tr>
<tr>
<td>Gerhardt</td>
<td>231, 187</td>
</tr>
<tr>
<td>Gersten</td>
<td>11, 131</td>
</tr>
<tr>
<td>Gerum</td>
<td>185, 188, 272</td>
</tr>
<tr>
<td>Gesnner</td>
<td>119</td>
</tr>
<tr>
<td>Gewecke</td>
<td>112</td>
</tr>
<tr>
<td>Ghosh</td>
<td>293, 299</td>
</tr>
<tr>
<td>Gialdini</td>
<td>253, 254</td>
</tr>
<tr>
<td>Giebelhausen</td>
<td>106, 134</td>
</tr>
<tr>
<td>Gibbs</td>
<td>49, 205, 231, 233, 252-254, 312</td>
</tr>
<tr>
<td>Gibson</td>
<td>67</td>
</tr>
<tr>
<td>Girard</td>
<td>65, 130</td>
</tr>
<tr>
<td>Gladstone</td>
<td>40, 43</td>
</tr>
<tr>
<td>Glaser</td>
<td>50</td>
</tr>
<tr>
<td>Glasser</td>
<td>52</td>
</tr>
<tr>
<td>Glatzel</td>
<td>129</td>
</tr>
<tr>
<td>Gmelin</td>
<td>43, 323</td>
</tr>
<tr>
<td>Goddfray</td>
<td>112, 197</td>
</tr>
<tr>
<td>Godon</td>
<td>94</td>
</tr>
<tr>
<td>Goldblum</td>
<td>45, 113, 114</td>
</tr>
</tbody>
</table>
NAME INDEX

Goldschmitt, 25
Goldstein, 264
Goloubkine, Mile, 164, 165
Gordon, 108
Gore, 196
Gorée, 49
Gowland, 83, 104, 259
Graham, 176-180, 187, 193
Grall, 324, 325, 328
Grampe, 200, 289, 341
Granger, 64, 127-129, 312
Greaves, 107
Grether, 132
Griffiths, 267
Groger, 58, 125, 286
Groh, 271
Groshans, 55, 123
Grossmann, 71, 72, 132
Groth, 311
Grotthus, 72
Grover, 266
Grube, 92, 268
Guertier, 27, 91, 107, 108, 133
Guillaumé, 91
Guilset, 90, 107-109
Gunter, 62, 126, 299
Gutbier, 137-147, 156, 161, 176, 184, 186, 191, 197-200, 209, 210, 316-318, 238, 245, 246, 270, 273, 274, 259, 289-300, 334, 336, 337
Gustavson, 76
Guyard, 329
Guyse, 95
Gwyer, 36, 107

Habas, 191
Haber, 209, 283
Habermann, 55, 63
Hacks, 155, 283
Hadow, 317, 318, 322, 323, 326
Hängi, 235
Hagenacker, 92
Hainbach, 100
Hainsworth, 34, 35, 100, 102
Halberstadt, 275, 298-300, 302
Hale, 93
Hall, 284
Hallett, 76
Hampe, 50, 126
Hansen, 50, 51
Hantzsche, 49, 291
Harbeck, 188, 274
Harder, 108
Hardin, 191
Harker, 263
Harper, 26-28, 35, 48
Harris, 76
Harrison, 91
Hartley, 43, 50
Hartmann, 185, 186
Haschek, 28, 92, 138, 155, 176, 209, 238, 263
Hatchett, 37, 108
Hauser, von, 54, 112, 123
Hauhofer, 133

Hautefeuille, 29, 64, 180, 265
Haynes, 36, 107
Hedvall, 48, 49, 74, 116
Heeren, 53
Hennich, 108, 193, 289
Helmolt, 38
Hempel, 32, 183
Henderson, 59, 260
Hennig, 176
Heraceus, 259, 267
Herrenschmidt, 22
Hertz, 69
Hess, 260
Higgs, 105, 109, 193, 194
Hiege, 37
Hendelmaier, 51, 117
Hirtzl, 51, 52
Horn, 105
Hitz, 66, 151
Hittorf, 17, 29, 93, 289
Hodgkinson, 283, 284
Höchlen, 132, 305
Hoffmann, 52, 258
Hoffmann, 51, 53, 117, 122, 132, 133, 221, 222, 306, 315
Hofmeier, 138, 145, 156, 184, 186, 210, 238, 273
Hohenegger, 186, 188
Hoffsema, 177, 180
Holborn, 91, 178, 263
Holland, 254
Holland, 118
Hollis, 93
Holm, 263
Holst, 326
Holt, 177, 188
Holtzmann, 256
Holzmann, 324
Honda, 27
Hoppe-Seyler, 157
Hostetter, 256, 287
Howe, 56, 137, 140, 142-144, 146-150, 152
Hoyer, 241
Hradecky, 205, 231, 283
Huber, 184
Hudson, 105
Hütter, 38, 109
Hansler, 71, 72
Hüttinger, 156, 158, 160, 163-165
Hütten, 50, 268
Huldschinsky, 77
Hulett, 267
Hunt, 192
Hussak, 174, 256

IciLius, 189
Ikeda, 272
Ilnsky, 75
Ingersoll, 155, 238
Ipatieff, 81, 93, 96, 111, 116, 122
Irman, 93, 109
Itzig, 205
Ivanov, 341

Jacobsen, 297
Jacoby, 127, 219
NAME INDEX

Jacquelain, 269
James, 71
Jamieson, 76, 135
Jannasch, 195, 334, 336
Jannen, 265
Jassoneix, du, 74, 133
Joannis, 196
Job, 51, 67
Jörgensen, 74, 133, 158, 166, 290, 294, 296, 297, 303
Johnson, 122, 135, 282
Jolibois, 128, 207
Jolin, 205, 324
Joly, 137–141, 146–148, 150, 151, 166, 167, 171, 184, 191, 209, 219, 231, 241, 244, 249, 253, 269
Jones, 67, 120, 131
Jorissen, 93
Joslin, 254, 312
Joule, 115
Jurgens, 94
Jurisch, 155, 157, 180, 192, 205

KAMMERER, 302
Kahibaum, 50, 262
Kahl, 272
Kalmus, 23–28, 35, 36, 47, 48
Kamm, 60
Kane, 122, 200, 204, 205
Kaneko, 91, 107
Karmrodt, 244
Kaye, 262, 264
Kayser, 264
Keferstein, 163, 244, 328
Keilg, 28, 66, 91, 131
Keiser, 175, 176, 189, 195
Kelber, 94, 96
Keller, 53, 203
Kemmerer, 190, 191
Kennott, 119
Kern, 206, 266
Kernot, 156, 293, 272
Kilian, 35, 110
Kimmins, 96, 270
Kirse, 279
Kirchhoff, 294
Klasson, 286, 287
Klobb, 53
Klobbie, 338
Kloss, 105
Knetsch, 268
Knocke, 4, 263
Knop, 316, 318
Knoirse, von, 75
Knot, 194
Kobbé, 158, 164, 169
König, 201
Kohlruschaus, 289
Kolffman, 237, 283
Könneck, de, 75, 119, 263
Konstantinoff, 37, 128
Kopa, 279
Kopp, 122
Koppel, 59–62, 70, 72
Korten, 246, 252, 254, 255

Kotschubei, 41
Krauss, 75, 299, 300
Kraut, 183
Krauter, 187
Krell, 189, 197–200
Krauss, 98
Krumhlaar, 92
Kunzel, 126
Kuhlmann, 266
Kubsch, 127
Kurnakooff, 108
Kuspert, 270

LABORD, 110
Laby, 262
Lachaud, 48, 53, 55, 123
Lacombe, 63, 127
Lamb, 189
Lampadius, 77
Lancien, 127, 156, 171
Lang, 126, 205, 244, 253, 254, 287, 307, 309, 310, 322
Lange, 98, 131
Langstein, 341
Lassaigne, 200, 247, 301, 302
Latschchenko, 281
Laurent, 127
Lautsch, 47
Lawrence, 263
Lea, Carey, 244, 287
Lebeau, 72, 73, 207, 254, 329
Ledent, 119
Lee, 81, 98
Lefevre, 65
Lefort, 132

Lehmann, 95, 100, 222
Leidlé, 151, 159–169, 191, 171, 173, 302, 236, 243, 244, 249, 253, 254, 340
Lenher, 50, 124, 131
Lepierre, 48, 53, 55, 123
Leroux, 131, 313
Lesour, 50, 54, 63, 122
Letts, 53
Leuchs, 146
Levi, 93
Levin, 108
Levy, 119, 284
Lewis, 41
Lewkonja, 36, 37, 66, 72, 73
Liebig, 21, 75, 307
Limmer, 269
Lind, 142, 150
Litton, 307
Liversidge, 79
Lockyer, 19, 79, 174, 235
Loew, 273
Loewenstamm, 288, 289
Loiseleur, 295
Loos, 131
Lorenz, 65
Lossew, 130
Louyet, 21
Lowe, 282
Lucchesi, 141, 142, 148, 149, 306
Luedert, 128
Luff, 128
Lunge, 188, 274
McCary, 265
McConnell, 50, 51
McDermott, 273
McElfresh, 179
McFarland, 108
MacGregor, 194
McLeod, 50
McMillan, 34, 100
Maddrell, 64, 128
Magnus, 26, 81, 263, 287
Mailfert, 202
Mailhè, 94
Maisch, 146, 165, 216, 273
Makowka, 336
Malagutti, 58
Mallet, 221
Manchot, 69, 153
Mansfeld, 26
Marchand, 97
Marguetti, 58, 64, 124
Margules, 307
Marie, 267, 268
Marignac, 30, 54, 62, 98, 110, 133, 244
Martin, 62, 92, 126, 131, 107, 201, 269, 283, 303, 305
Martus, 172, 233, 234, 254, 255, 316, 318, 319, 321-326
Mathes, 302
Matthews, 70, 71
Matthey, 158, 235, 254, 261, 281
Mattheson, 193, 194
Mauener, 293
Mawrow, 50
Maxted, 188
Mayer, 51, 92, 334
Mazzetti, 108
Mazzucchelli, 332, 340
Meigen, 45, 55, 67, 94, 95
Meitendorff, 71, 133
Mellor, 77, 135, 344
Memminger, 267
Mendenhall, 155, 238
Meneghini, 118
Merrick, 111
Metz, 180, 192
Metz, 50, 68, 76
Meusser, 45, 46, 113-115
Meyer, A. R., 265
Meyer, E. von, 229, 307
Meyer, J., 53, 266
Meyer, R. J., 42, 127
Meyer, V., 267, 281, 283, 298
Mietzschke, 242
Miller, 70, 71, 282
Mills, 47
Mingaye, 341

NAME INDEX
Minozzi, 308
Miolaìi, 142, 143, 148, 253, 254, 288, 290, 297, 300, 303
Mitchell, 111
Mitscherlich, 122
Moeser, 11
Monk, 24, 66, 87, 98, 131, 151, 178, 187, 188
Moore, 118, 135
Morahit, 210, 213, 215, 217-220, 228, 229
Morgan, 93
Morrell, 77
Mosnier, 44
Moureu, 29, 94
Mourlot, 51, 110
Muller, 45, 55, 77, 92, 118, 259, 300
Murnmann, 290
Muspratt, 52, 120, 121, 124
Mylius, 138, 266, 313-315, 332, 340, 343
NANTY, 67, 132
Naumann, 42
Neall, O', 56
Neogi, 93, 94
Neuburger, 37
Neumann, 27, 29
Neundlinger, 274
Neville, 108, 109, 193, 194
Newlands, 2
Newth, 178, 179
Nicklès, 29, 92
Nikolaus, 267
Nilson, 57, 124, 285-288, 295, 300-311
Niquesa, 272
Nola, dì, 103, 134
Nordenskold, 196
Normann, 95, 134, 222
Norton, 288, 290, 296
Novitzky, 329
OHL, 119
Oppius, 247
Orôway, 62
Orloff, 174, 222, 333, 338
Oueta, de, 256
Osann, 136
Ostwald, 40, 96
Ottenstein, 187
Ouvrard, 74, 129, 134
PALL, 6, 96, 117, 156, 184-188, 195, 210, 238, 239, 268, 270, 272, 273, 336, 338
Palmer, 122
Parker, 272
Parr, 107
Parravano, 17, 108, 275, 293, 305
Pashsky, 193
Patéra, 21, 87
Patrick, 301
Pelal, 51
Pelletier, 26
Pelleter, 312
<table>
<thead>
<tr>
<th>NAME</th>
<th>INDEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellini,</td>
<td>118</td>
</tr>
<tr>
<td>Pendini,</td>
<td>288</td>
</tr>
<tr>
<td>Penfield,</td>
<td>257</td>
</tr>
<tr>
<td>Perkin,</td>
<td>60, 61</td>
</tr>
<tr>
<td>Peters,</td>
<td>116, 188</td>
</tr>
<tr>
<td>Peterson,</td>
<td>341</td>
</tr>
<tr>
<td>Petit,</td>
<td>263</td>
</tr>
<tr>
<td>Petit, J.,</td>
<td>317, 320</td>
</tr>
<tr>
<td>Petrenko,</td>
<td>37, 109</td>
</tr>
<tr>
<td>Petrenko-Kritschenko,</td>
<td>203</td>
</tr>
<tr>
<td>Pfennig,</td>
<td>76</td>
</tr>
<tr>
<td>Philipp,</td>
<td>259</td>
</tr>
<tr>
<td>Philipp,</td>
<td>121, 122, 141, 161, 183, 196, 210, 229, 290</td>
</tr>
<tr>
<td>Piocini,</td>
<td>170</td>
</tr>
<tr>
<td>Pickering,</td>
<td>12</td>
</tr>
<tr>
<td>Pichon,</td>
<td>28, 29</td>
</tr>
<tr>
<td>Pirani,</td>
<td>265</td>
</tr>
<tr>
<td>Pitkin,</td>
<td>303</td>
</tr>
<tr>
<td>Playfair,</td>
<td>39, 53, 54, 115</td>
</tr>
<tr>
<td>Podkopeeff,</td>
<td>284</td>
</tr>
<tr>
<td>Pontio,</td>
<td>103</td>
</tr>
<tr>
<td>Portevin,</td>
<td>108</td>
</tr>
<tr>
<td>Potain,</td>
<td>196</td>
</tr>
<tr>
<td>Potilitzin,</td>
<td>39, 40</td>
</tr>
<tr>
<td>Pouget,</td>
<td>66, 110</td>
</tr>
<tr>
<td>Poulenc,</td>
<td>38, 110</td>
</tr>
<tr>
<td>Pozzi-Escot,</td>
<td>205</td>
</tr>
<tr>
<td>Prausnitz,</td>
<td>341</td>
</tr>
<tr>
<td>Pretenius,</td>
<td>58</td>
</tr>
<tr>
<td>Price,</td>
<td>270–272</td>
</tr>
<tr>
<td>Prinz,</td>
<td>238</td>
</tr>
<tr>
<td>Proust,</td>
<td>20</td>
</tr>
<tr>
<td>Pullinger,</td>
<td>280, 296–298, 301, 314</td>
</tr>
<tr>
<td>Pungs,</td>
<td>95</td>
</tr>
<tr>
<td>Purgotti,</td>
<td>274</td>
</tr>
<tr>
<td>Pushin,</td>
<td>37, 66, 109, 130, 193, 281</td>
</tr>
<tr>
<td>QUADRAT,</td>
<td>316, 319, 322, 325</td>
</tr>
<tr>
<td>Quesnens,</td>
<td>155, 202, 253, 254, 265, 339, 340</td>
</tr>
<tr>
<td>Quennessen,</td>
<td>21</td>
</tr>
<tr>
<td>Quincke,</td>
<td>98, 131</td>
</tr>
<tr>
<td>RACK,</td>
<td>134</td>
</tr>
<tr>
<td>Rammelsberg,</td>
<td>42, 44, 46, 47, 49, 52, 53, 64, 68, 113, 114, 120, 121, 128, 206</td>
</tr>
<tr>
<td>Ramsay,</td>
<td>176–178, 182, 187, 188, 294</td>
</tr>
<tr>
<td>Randall,</td>
<td>264</td>
</tr>
<tr>
<td>Ranvier,</td>
<td>147</td>
</tr>
<tr>
<td>Ranzhoff,</td>
<td>144–147</td>
</tr>
<tr>
<td>Raphe,</td>
<td>108</td>
</tr>
<tr>
<td>Rath, von,</td>
<td>124</td>
</tr>
<tr>
<td>Rathert,</td>
<td>92</td>
</tr>
<tr>
<td>Rathiburg,</td>
<td>219</td>
</tr>
<tr>
<td>Ray,</td>
<td>60, 293, 299</td>
</tr>
<tr>
<td>Rayzt,</td>
<td>37</td>
</tr>
<tr>
<td>Raynaud,</td>
<td>42, 112</td>
</tr>
<tr>
<td>Read,</td>
<td>49, 107</td>
</tr>
<tr>
<td>Regnault,</td>
<td>28, 29, 155, 176, 209, 238, 263</td>
</tr>
<tr>
<td>Reichard,</td>
<td>65, 126, 130, 312</td>
</tr>
<tr>
<td>Reichardt,</td>
<td>37</td>
</tr>
<tr>
<td>Reichenstein,</td>
<td>93</td>
</tr>
<tr>
<td>Reinsch,</td>
<td>53</td>
</tr>
<tr>
<td>Reiss,</td>
<td>334</td>
</tr>
<tr>
<td>Remele,</td>
<td>48</td>
</tr>
<tr>
<td>Remmler,</td>
<td>32</td>
</tr>
<tr>
<td>Renz,</td>
<td>158, 322</td>
</tr>
<tr>
<td>Reusch,</td>
<td>122</td>
</tr>
<tr>
<td>Reynolds,</td>
<td>326, 327</td>
</tr>
<tr>
<td>Reynoso,</td>
<td>130</td>
</tr>
<tr>
<td>Rhead,</td>
<td>135</td>
</tr>
<tr>
<td>Rachards,</td>
<td>29, 32, 33, 42, 97, 111, 112, 116</td>
</tr>
<tr>
<td>Richardson,</td>
<td>177</td>
</tr>
<tr>
<td>Richer,</td>
<td>110</td>
</tr>
<tr>
<td>Richter,</td>
<td>80</td>
</tr>
<tr>
<td>Riedel,</td>
<td>90, 115, 123</td>
</tr>
<tr>
<td>Rieth,</td>
<td>39</td>
</tr>
<tr>
<td>Riewend,</td>
<td>163</td>
</tr>
<tr>
<td>Rigg,</td>
<td>99</td>
</tr>
<tr>
<td>Rimbach,</td>
<td>38, 110, 246, 252, 254, 255</td>
</tr>
<tr>
<td>Runmann,</td>
<td>48</td>
</tr>
<tr>
<td>Rio, del,</td>
<td>154</td>
</tr>
<tr>
<td>Rissom,</td>
<td>59, 125</td>
</tr>
<tr>
<td>Roberts,</td>
<td>4, 176, 264</td>
</tr>
<tr>
<td>Roberts-Austen,</td>
<td>87</td>
</tr>
<tr>
<td>Robin,</td>
<td>107</td>
</tr>
<tr>
<td>Röhrig,</td>
<td>52, 120, 121</td>
</tr>
<tr>
<td>Rössler, C.,</td>
<td>76</td>
</tr>
<tr>
<td>Rössler, F.,</td>
<td>194, 203, 204, 206, 306, 308, 309, 313</td>
</tr>
<tr>
<td>Rössler, H.,</td>
<td>159, 206, 316</td>
</tr>
<tr>
<td>Rogers,</td>
<td>82, 116, 309</td>
</tr>
<tr>
<td>Root,</td>
<td>50</td>
</tr>
<tr>
<td>Rossler,</td>
<td>259</td>
</tr>
<tr>
<td>Rose,</td>
<td>39, 47, 53, 64, 67, 90, 119, 132, 134, 222, 238</td>
</tr>
<tr>
<td>Rossell,</td>
<td>11</td>
</tr>
<tr>
<td>Rosenbladt,</td>
<td>61</td>
</tr>
<tr>
<td>Rossi,</td>
<td>8, 68, 132</td>
</tr>
<tr>
<td>Rossignol,</td>
<td>210</td>
</tr>
<tr>
<td>Rostosky,</td>
<td>195, 336</td>
</tr>
<tr>
<td>Roth,</td>
<td>186</td>
</tr>
<tr>
<td>Rothberg,</td>
<td>7</td>
</tr>
<tr>
<td>Rother,</td>
<td>238, 242</td>
</tr>
<tr>
<td>Rothoff,</td>
<td>97</td>
</tr>
<tr>
<td>Rotter,</td>
<td>320</td>
</tr>
<tr>
<td>Rouh,</td>
<td>279</td>
</tr>
<tr>
<td>Rousseau,</td>
<td>51, 74, 127, 134</td>
</tr>
<tr>
<td>Rousin,</td>
<td>26</td>
</tr>
<tr>
<td>Rubegni,</td>
<td>117</td>
</tr>
<tr>
<td>Rubes, de,</td>
<td>256, 257</td>
</tr>
<tr>
<td>Rudnick,</td>
<td>274, 291</td>
</tr>
<tr>
<td>Rübenkamp,</td>
<td>48, 73</td>
</tr>
<tr>
<td>Ruer,</td>
<td>91, 107, 192, 193, 268, 269</td>
</tr>
<tr>
<td>Rupp,</td>
<td>76</td>
</tr>
<tr>
<td>Russell,</td>
<td>39, 40, 48, 98, 273</td>
</tr>
<tr>
<td>Rykowkoff,</td>
<td>108</td>
</tr>
<tr>
<td>Sabattier,</td>
<td>29, 39, 48, 59, 93–95, 115, 116, 126</td>
</tr>
<tr>
<td>Sachs,</td>
<td>217</td>
</tr>
<tr>
<td>Sack,</td>
<td>253</td>
</tr>
<tr>
<td>Sadler,</td>
<td>60</td>
</tr>
</tbody>
</table>
Sahme, 37
St. Edme, 29, 59
St. Evre, 60
Sale, 155, 157, 159, 242, 264, 342
Salkowski, 17, 93, 266, 289
Salvadori, 40, 45, 113
Saltzat, 123
Sand, 280
Sander, 206
Sargent, 135
Sarzeau, 58
Sasserath, 216-218, 223, 230
Savell, 35
Scaghanai, 184, 195, 198
Schalank, 316, 319, 325
Scheibler, 295
Scheaitsehnschay, 37, 64, 108
Scheak, 127
Sehepeleff, 64
Scheurer, 19
Sehick, 222
Scheitf, 40, 54, 111
ScMmizu, 27
Schirmeister, 36, 107
Schlegelmilch, 42
Schlossberger, 117
Schmitt, 28, 92
Schmitz, 28
Sehaedermaaa, 307, 319
Schneider, 30, 31, 52, 95, 98, 201, 203, 204, 222, 306, 307, 329
Schoch, 93, 101
Schönlein, 157, 238
Schoitz, 322
Schonfeld, 134
Schorlemmer, 259
Schottländer, 307
Schröder, 47, 60, 115, 118
Schrötter, 324
Schultzeberg, 98, 111, 265, 267, 284, 312-314
Schulten, de, 49, 117
Schulte, 278
Schultze, 125
Schulze, 52, 58, 117
Schumann, 48, 51
Schurigin, 151, 205
Schwarz, 127, 186, 272
Schwarzenberg, 49, 51, 120
Scott, 55
Seamon, 174
Sodell, 54, 294
Senarmont, de, 52, 67, 119
Senderens, 29, 48, 59, 66, 93-95, 115, 116, 126, 130
Senglet, 92, 131
Senter, 268
Setterberg, 52, 67
Seubert, 39, 52, 121, 158, 164, 169, 211, 216, 240, 243, 248, 251, 275, 276
Seybolt, 212
Sharswood, 26
Shields, 178, 187, 188
Shinn, 72, 190, 192
Sleurs, 92, 156, 157, 178-182, 188, 265
Silvester, 85
Sisson, 322
Skey, 77, 327
Smith, 273
Smith, D. P., 108
Smith, E. A., 283
Smith, E. F., 189, 199, 203
Smoot, 336
Soerensen, 23, 111
Sonmaruga, 31, 98
Sonnenfeld, 210
Sonnenhahn, 125
Sosnan, 91, 157, 159, 176, 256, 267
Spear, 272
Spiller, 282
Spitzer, 92
Steele, 122
Steinmann, 282
Stodart, 212, 263
Stokes, 318
Stolba, 263
Strecker, 151, 205
Streicher, 242, 243, 245, 285, 289
Streintz, 29
Strengers, 7, 138, 157, 239, 275
Struve, 212, 231, 232
Stuchlik, 307
Sturm, 90, 262
Sule, 209
Suzuki, 59
Svanberg, 221

TAEssaert, 20
Tafel, 108, 109
Tagiuri, 142, 143, 148
Tamann, 27, 37, 91, 107, 108, 133, 194
Tanatar, 274
Tarugi, 40, 284
Taylor, 47
Teichmann, 116
Tennant, 208, 212, 213, 222, 235, 242
Terlikowski, 45, 113, 114
Terrell, 120
Thénard, 20, 210
Thiel, 119
Thiele, 32
Thoma, 178
Thompson, F. C., 105
Thompson, J. F., 282
Thompson, S., 34
Thomsen, 286, 287, 292, 295, 298
Thomson, 163, 245
Thorpe, 53-55, 151
Thüringer, 336, 345
Tibbals, 58, 124
Tibbals, 40
Tilden, 27, 28, 54, 178
Tingle, A., 291
Tingle, J. B., 291
Tite, 127
Tivoli, 312
Tobler, 64-66, 123
Tollens, 71
Tolman, 82
NAME INDEX 355

Topsoe, 57, 70, 73, 198, 300–302, 304, 310, 311, 319
Travers, 177, 264
Treadwell, 72, 77
Trenkner, 137, 140, 143, 144, 147
Trommsdorff, 21
Troost, 29, 180, 265
Trottarelli, 174
Tsichrov, 213, 221
Tschugaev, 115, 119, 222, 338
Tubandt, 29, 109, 115, 123
Tutton, 27, 55, 91, 123, 124

UHRLAUB, 244
Ulke, 87
Ulrik, 58
Urazov, 108

VAILLANT, 41
Valentiner, 187
Vavon, 273
Verger, du, 339
Veaces, 151, 206, 209, 286, 287, 310, 311
Vigouroux, 72, 108, 109, 129, 130, 133, 329
Villiers, 119
Villiger, 69
Vincent, 163
Violette, 263
Violle, 176, 238, 263
Vogel, 77
Vogt, 139
Vorster, 48, 115
Vortmann, 50, 54, 55
Voss, 107–109

WACHTER, 45, 113
Waelhert, 108
Wagener, 71
Wagner, 270
Wahl, 37
Waldner, 263
Walden, 72, 133
Walker, 50, 78, 257
Wallace, 199
Waltenberg, 91, 155, 242, 264, 280
Wanjukow, 53, 122
Ward, 135
Waring, 281, 284
Watts, 34, 35–35, 102, 121
Weber, 289, 291, 309
Weil, 58, 124
Weinland, 42
Weinschenk, 51, 119
Weissberg, 69
Welkow, 198, 295
Wells, 72, 133, 257

Werner, 30, 42, 43, 91, 232
Wernicke, 50, 72
Wertheim, 184
Weselsky, 31, 69, 318
Weyde, 238
White, 263
Wicke, 118
Wiede, 133
Wien, 91, 176, 263
Wiggersmann, 146
Wild, 69
Wilde, de, 268
Willand, 71
Wilm, 155, 157, 163, 165, 172, 200, 201, 323, 325
Willstätter, 210
Wilson, 84
Windisch, 268
Winkelblech, 48, 50, 63, 67
Winkelmann, 177, 264
Winkler, 26, 27, 31, 32, 76, 90, 98, 133, 329
Wintrebert, 216, 218, 219, 223–228, 232, 233
Wischir, 210, 213, 215, 217, 218, 220, 228, 229
Witt, de, 21
Wittstein, 263
Witzmann, 248, 249
Wohl, 26
Wolff, 77
Wollaston, 154, 155, 172, 174, 196, 197, 205, 206
Wood, 60, 61, 67
Wreweisky, 40
Wright, 50
Wunder, 336, 345
Wurtz, 54
Wurzer, 1
Wyrouboff, 40, 328

ZAMBOJNINI, 306
Zanichelli, 274
Zappi, 266, 268, 287, 291, 334, 340
Zdrawkowitch, 273
Zeise, 273
Zemczuzny, 108
Zerr, 48, 73
Zimmermann, 31, 49, 98
Zsigmondy, 185, 270
Züblin, 298
Zurcker, 143, 144
Zwenger, 69, 70

YAMASAKI, 268
SUBJECT INDEX

Alum, cobalt, 56
iridium, 251
rhodium, 169
Aluminium chlorpalladite, 197
chlorplatinate, 295
platinocyanide, 319
Ammonium brom-iridate, 247
brom-iridite, 247
bromosmate, 218
brompalladate, 200
brompalladite, 199
bromplatinate, 299
bromruthenate, 144
bromruthenite, 144
calcium platinocyanide, 321
chlor-iridate, 246
chlor-iridite, 244
chlorosmate, 216
chlorosnite, 215
chlorpalladate, 198
chlorpalladite, 196
chlorpalladosulphite, 204
chlorplatinate, 293
chlor-ruthenate, 143
cobalt alum, 56
cobalt chromate, 58
cobalt sulphate, 55
cobalt sulphite, 52
cobalticyanide, 69
cobaltinitrite, 61
hexachlor-rhodite, 163
iodiridate, 247
iodiridite, 247
iodoplatinate, 302
iodosmate, 218
iridinitrite, 253
iridium alum, 251
iridium sulphite, 251
nickel chloride, 111
nickel chromate, 125
nickel selenate, 124
nickel sulphate, 123
nickel sulphite, 121
nitroso-chlor-ruthenate, 150
osminitrite, 233
osmyl bromide, 225
chloride, 225
osmyloxy-bromide, 227
osmyloxy-chloride, 227
osmyloxy-nitrite, 228
palladocyannide, 206
pentabrom-rhodite, 164
pentachlor-rhodite, 163
Ammonium platinocyanide, 319
platinonitrite, 309
rhodichlor-nitrate, 171
rhodinitrate, 171
rhodium alum, 170
selenocyanoplatinite, 328
tetrachlorplatinite, 287
thiocyanoplatinite, 328
thiocyanoplatinum, 328
Annabergite, 79, 80, 130
Aquochl-or-ridites, 244
Argozoul, 106
Asbolan, 19, 20
Asbolite, 20
Asymmetry of cobalt, 30
Barium brompalladite, 199
bromplatinate, 300
chlor-iridate, 244
chlorpalladite, 197
chlorplatinate, 295
cobalticyanide, 69
cobaltinitrite, 61
red, 62
cobaltite, 51
dicobaltite, 51
iodoplatinate, 302
iridicyanide, 255
iridium chlor-nitrite, 254
nickelite, 117
osmate, 220
osmamate, 232
osminitrite, 233
osmoxyanide, 234
osmyloxy-nitrite, 228
pentabromrhodite, 165
pentachlorhydroxyplatinate, 296
platinocyanide, 319
potassium osmocyanide, 234
potassium platinocyanide, 324
radium platinocyanide, 324
rhodinitrite, 171
rutenate, 147
ruthenite, 146
ruthenocyanide, 152
tetrachlorplatinite, 287
thiocyanoplatinate, 328
Benedict metal, 104
Bessemierised matte, 83
Bieberite, 20, 54
Bismuth ruthenocyanide, 153
Bismuto-smaltite, 19, 20
Black nickel, 79, 80

356
Blueite, 78, 80
Breihauptite, 78, 80
Bromiridates, 247
Bromiridites, 247
Bromosmates, 217
Bromoplattadates, 199
Bromoplattadites, 199
Bromochloroplatinates, 299
Bromoplatinic acid, 298
Bromoplatinous acid, 298
Bromrhodites, 164
Bromruthenates, 144
Bromruthenites, 144
Browne's Process, 79
Bunsenite, 79, 80, 115

CADMIUM chlorpalladite, 197
chlorplatinate, 295
platinonitrite, 310
ruthenocyanide, 152
tetrachlor-dihydroxyplatinate, 296

Cesium aquochlor-ruthenate, 142, 143
bromoplattadate, 200
bromoplattadite, 199
bromoplatinate, 300
bromruthenate, 144
bromruthenite, 144
chlor-iridate, 246
chlor-iridite, 244
chlorosmate, 216
chloroplattadate, 198
chloroplattadite, 197
chlorplatinate, 293
chlor-ruthenate, 143
chlor-ruthenite, 142
cobalt alum, 56
chromate, 58
iridium alum, 252
chlor-nitrite, 254
nickel chromate, 125
chloride, 112
selenate, 124
sulphate, 123
nitroschlor-ruthenate, 150
oxychlor-ruthenate, 143
pentachlorplatinite, 288
pentabromrhodite, 164
pentachlor-rhodite, 163
platinonitrite, 310
rhodium alum, 170
tetrachlorplatinite, 287

Calcium ammonium platinocyanide, 321
bromplatinate, 300
chlorplattadite, 197
chlorplatinate, 295
iodoplatinate, 302
osmintrite, 233
platinoycyanide, 321
platinonitrite, 310
potassium platinocyanide, 321
ruthenate, 147
tetrachlorplatinite, 287

Carbonyl platinum monoxide, 315
mono sulphide, 315
thiocarbonate, 315
thiocyanate, 315
Carrollite, 19, 20
Cerium chlorplatinate, 295
platinocyanide, 321
tetrachlorplatinite, 287
Chloanthite, 19, 78, 80, 129
Chlorhydroxyplatinic acids, 296
Chlor-iridates, 245
Chlor-iridites, 243
Chlorosmates, 216
Chlorosmites, 215
Chloroplattadates, 197
Chloroplattadites, 196
Chlorplatinates, 292
Chlorplatinites, 286
Chlor-rhodates, 162
Chlor-ruthenates, 142
Chlor-ruthenites, 141
Chromium nickel, 107
Cobalt. See Chap. II
asymmetry, 30
atomic weight, 30-33
chemical properties, 29-30
comparison with iridium, 14-15
iron, 7-10
nickel, 7-10
rhodium, 14-15
detection, 74
electrodeposition, 34
electrolytic preparation, 25
estimation, 75
history, 19
laboratory preparation, 26
nitro, 59
occlusion of hydrogen, 28
occurrence, 19
ores, 19
passivity, 7, 29
physical constants, 5, 26-28
properties, 26
preparation, 20-25
presence in sun, 19
pyrophoric, 26
tables of compounds, 10, 15
uses, 33
volatilisation, 4
white, 19
Cobalt alloys, 36-37
alums, 56-57
ammonium, 56
cesium, 56
potassium, 56
rubidium, 56
ammonium sulphate, 55
solubility of, 55
ammonium sulphite, 52
antimonate, 66
antimonides, 66
arsenates, 65
arsenides, 65
arsenite, 65
azoimide, 59
bloom, 19, 20, 65
Cobaltic chloride, 42
fluoride, 38
nitrate, 63
oxide, 50
selenite, 57
sulphate, 58
sulphide, 52
Cobaltite, 19, 20
Cobaltites, 51
Cobalto-cobaltic oxide, 49
Cobalto-cobalti-trinitrite, 62
Cobaltocyanides, 68
Cobaltous acid, 51
Cobaltous salts. See Cobalt
Chromite, 36
Constantan, 106
Copper bromplatinate, 300
chlorplatinate, 295
cobalt sulphate, 55
cobalticyanide, 70
nickel, 78, 80
platinocyanide, 321
platinonitrite, 310
ruthenocyanide, 152
tetrachlorplatinate, 287
Cupronickel, 104
Cyanoplatinites, 326
Cyanoplatinites, 316
Cyanoplatinocyanide, 326
Cyanoplatinous acid, 316
Dental alloy, 283
Dicarbonylplatinum dichloride, 314
Dichloridihydroxyplatinic acid, 288
Dichloridihydroxyplatinum acid, 288
Dichlorocyanoplatinitic acid, 326
Dichloropalladous acid, 196
Dicobaltites, 61
Dicobalt pentarsenide, 65
Dinickel phospide, 127
Dinickel silicide, 133
Diphosgene platinum dichloride, 314
Dirodium pentoxide, 167
Driers, cobalt, 34
Earthly cobalt, 19, 20
Emerald nickel, 79, 80
Erythine, 20
Erythrite, 19, 20, 65
Eugenesite, 174
Ferrous cobalticyanide, 70
Fischer’s nitrite process, 24
salt, 60, 70, 75
Folgerite, 78, 80
Gadolinium chlorplatinate, 295
Garnierite, 79–81
analysis, 82
Genthite, 79
German silver, 104
Gersdorffite, 78, 80
Glaucodote, 19
Glucinium chlorplatinic acid, 295
tetrachlorplatinic acid, 287
Goldschmidt’s method, 25
Gmelin’s salt, 323
Halogen cyanoplatinites, 326
nitroplatinates, 311
nitroplatinites, 311
Hardening of oils, 95
Herrenschmidt’s method, 22
Hexabromplatinitates, 199
Hexabrom-iridates, 247
Hexabrom-iridites, 247
Hexabrom-platinates, 217
Hexabrom-platininites, 299
Hexabrom-ruthenates, 144
Hexachlor-iridates, 245
Hexachlor-iridites, 243
Hexachlor-osmates, 216
Hexachlor-osmites, 215
Hexachlor-palladates, 197
Hexachlor-platinates, 292
Hexachlor-platinic acid, 290
Hexachlor rhodites, 162
Hexachlor-ruthenates, 142
Hexahydroxy-platinic acid, 304
Hexa-iodiridates, 247
Hexa-iodidrites, 247
Hexa-iodoplatinates, 302
Hexa-iodosmates, 218
Hybinette Process, 89
Hydrogen cobalticyanide, 68
iridicyanide, 254
iridinitrite, 252
oxmocyanide, 233
tetramtroplatinite, 309
Hydrazine platinocyanide, 322
Hydrogenation of oils, 95
Hydroxylamine platinocyanide, 322
Igneous, 107
Indium chlorplatinate, 295
platinocyanide, 322
Ink, sympathetic, 42, 34
Invar, 103
Iodidrites, 247
Iodidrites, 247
Iodoplatinates, 305
Iodoplatinous acid, 301
Iodosmates, 218
Iridium. See Chap. VIII
absorption of hydrogen, 238
atomic weight, 3, 240
chemical properties, 239
colloidal, 6, 238
comparison with cobalt and rhodium, 14
detection, 7, 339
estimation, 339
explosive, 239
history, 235
occurrence, 235
physical constants, 5
physical properties, 237
preparation, 235
presence in sun, 235
purification, 235
Iridium, separation from platinum metals, 342-345
tables of compounds, 15
uses, 241
volatilisation, 4, 5, 264, 280

Iridium alloys, 241
alums, 251
amalgam, 242
ammonium sulphite, 251
black, 238
bromides, 246
chlorides, 242
chlorinitrites, 253
cyane, 254
dichloride, 242
di-oxyde, 248
colloidal, 249
hydrated, 249
disulphate, 252
dihydrosol, 6, 258
iodides, 247
monochloride, 242
monosulphide, 250
monoxide, 248
oxybromide, 247
phosphide, 254
potassium sulphate, 250
sesquioxide, 248
sesquiselenide, 252
sesquisulphate, 251
sesquisulphide, 250
sesquisulphite, 250
tetrahbromide, 247
tetrachloride, 244
tetra-iodide, 247
tribromide, 246
acid, 247
trichloride, 243
tri-iodide, 247
tri-oxyde, 249

Iridosmine, 208

Iron, comparison with manganese, 11
nickel and cobalt, 7
ruthenium and osmium, 12
physical constants, 5
table of compounds, 10
volatility, 4
Iron chlorplatinate, 287
dioplatinate, 302
tetrachlorplatinate, 287

JAIPURITE, 19, 20, 51

KINO'S blue, 48
Kupfernickel, 79, 80

LAVURITE, 136
Lead bromplatinate, 300
chlorplatinate, 295
cobaltcyanide, 71
iridium chlorinitrite, 254
pentachlorhydroxyplatinate, 296
platinocyanide, 322
platinonitrile, 310
ruthenocyanide, 152
tetrabromohydroxyplatinate, 300

Lead tetrachlorohydroxyplatinate, 296
tetra-iodohydroxyplatinate, 302
thiocyanoplatinate, 328
trichlorohydroxyplatinate, 288

Liebig's method, 21, 75
Lunseite, 19, 20, 79, 80
Lithium chlorplatinate, 295
nickel chloride, 111
platinocyanide, 326
platinocyanide, 322
platinonitrile, 310
potassium platinocyanide, 234

Magnesium bromplatinate, 300
chlorpalladate, 198
chlorpalladite, 197
chlorplatinate, 295
cobaltite, 51
iodoplatinate, 302
osminitrite, 233
platinocyanide, 322
platinonitrile, 310
ruthenate, 147
tetrachlorplatinate, 287

Manganese brompalladite, 199
bromplatinate, 300
chlorpalladate, 198
chlorpalladite, 197
chlorplatinate, 295
iodoplatinate, 302
platinonitrile, 310
ruthenocyanide, 153

Manganin, 106
Maucherte, 78
Melonite, 78, 80, 124
Mercury iridium chlorinitrite, 254
platinocyanide, 323
ruthenocyanide, 153
tetrabromohydroxyplatinate, 300
tetra-iodohydroxyplatinate, 302

Millerite, 78, 80, 119
Molybdenum-nickel, 107
Mond process, 24, 87
Monochlorpentahydroxyplatinic acid, 297
Monocarbonyl platinum dichloride, 313
Moresonite, 78, 80, 121

NATURAL alloys, 104
Nevyanskite, 235
Niccolite, 78-80, 129
Nichrome, 106
Nickel. See Chap. III
atomic weight, 96-99
black, 79
catalytic, 93
chemical properties, 93-95
collodial, 96
commercial production, 81-90
comparison with coobalt, 7-10
copper, 12
iron, 7-10
palladium, 16-18
platinum, 16-18
detection, 134
electrodeposition, 99, 100-103
Nickel, electrolytic preparation, 89
emerald, 79
estimation, 134
history, 79
laboratory preparation, 81
metallurgy, 83-89
occlusion of hydrogen, 92
occurrence, 78
ores, 78-82
passivity, 7, 92, 101
physical constants, 5, 90-92
properties, 90-93
physiological action, 95
presence in sun, 79
pyrophoric, 96
sources, 81
tables of compounds, 10, 17
uses, 99
volatilisation, 4
white, 78
Nickel alloys, 103-109
amide, 125
ammonium chloride, 111
chromate, 125
selenate, 124
sulphate, 123
antimonate, 130
antimonide, 130
arsenate, 130
arsenides, 129
arsenito, 130
azomide, 125
blende, 78
bloom, 79, 80
borates, 134
borides, 133
brass, 104
bromate, 114
bromide, 112
bromplatinate, 300
bronze, 99, 104
cassium chlorides, 112
chromate, 125
selenate, 124
sulphate, 125
carbide, 92, 131
carbonate, 132
carbonyl, 131
clorate, 113
cloride, 111
clorostannate, 133
cloropalladate, 198
cloropalladite, 197
clorplatinate, 295
cromate, 124
basic, 124
cromium, 107
cobalt sulphate, 55
cobalticyanide, 71
cobaltocyanide, 68
compounds, 109
currency, 99
cyanide, 132
di-arsenide, 129
di-borate, 134
di-boride, 134
Nickel di-chromate, 125
di-hydroxide, 116
di-oxide, 117
di-phosphide, 128
di-selenide, 123
di-sulphide, 120
fluoride, 110
fluosilicate, 133
fluostannate, 133
halides, 110
hexametaphosphate, 128
hydroxide, 116
hypophosphite, 128
iodate, 114
hydrates, 114, 115
iodoplatinate, 302
iodide, 113
lithium chloride, 111
mats, 83
metaphosphate, 128
molybdate, 125
molybdenum, 107
monantimonide, 130
monarsenide, 129
monocyanide, 132
monoboride, 133
monoselenide, 123
monosilicide, 133
monosulphide, 119
monoteluride, 124
monoxide, 115
nitrate, 126
nitride, 125
nitrite, 126
ochre, 85, 80
ortho-arsenate, 130
ortho-phosphate, 128
orthosilicite, 133
oxides, 115
perchlorate, 113
per-iodates, 115
peroxide, 118
phosphates, 128
phosphides, 127
phosphites, 128
platinonitrite, 310
potassium azomide, 125
chromate, 125
nitrite, 126
selenate, 124
sulphate, 123
pyrites, 78
pyrophosphate, 129
rubidium chloride, 112
chromate, 125
selenate, 124
sulphate, 123
ruthenocyanide, 153
salts, cobalt free, 110
selenate, 124
selenide, 123
selenite, 123
sesquioxide, 117
sesquiphosphate, 128
sesquiselenide, 123
sesquisulphide, 120
<table>
<thead>
<tr>
<th>Subject Index</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sesquitelluride, 124</td>
<td><strong>Osmium, colloidal, 210</strong></td>
<td>comparison with iron and ruthenium, 12</td>
<td></td>
</tr>
<tr>
<td>silicates, 133</td>
<td>detection, 337</td>
<td>estimation, 338</td>
<td></td>
</tr>
<tr>
<td>silicides, 133</td>
<td>history, 208</td>
<td>occurrence, 208</td>
<td></td>
</tr>
<tr>
<td>silver, 80, 105</td>
<td>physical constant, 5</td>
<td>properties, 200</td>
<td></td>
</tr>
<tr>
<td>stannate, 133</td>
<td>preparation, 208</td>
<td>recovery of, 209</td>
<td></td>
</tr>
<tr>
<td>steel, 103</td>
<td>separation from platinum metals, 342–346</td>
<td>table of compounds, 13</td>
<td></td>
</tr>
<tr>
<td>stibine, 79</td>
<td>uses, 212</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sub-boride, 134</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sub-phosphide, 127</td>
<td><strong>Osmium alloys, 212</strong></td>
<td>bromides, 217</td>
<td></td>
</tr>
<tr>
<td>sub-oxide, 115</td>
<td>chlorides, 214</td>
<td>cyanide, 223</td>
<td></td>
</tr>
<tr>
<td>sub-selenide, 123</td>
<td>diammine hydroxide, 231</td>
<td>dichloride, 214</td>
<td></td>
</tr>
<tr>
<td>sub-silicide, 133</td>
<td>dihydroxide, 219</td>
<td>di-oxide, 219</td>
<td></td>
</tr>
<tr>
<td>sub-sulphide, 119</td>
<td>hydrated, 219</td>
<td>pyrophoric, 219</td>
<td></td>
</tr>
<tr>
<td>sulphate, 78, 121</td>
<td>colloidal, 220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulphides, 119</td>
<td>disulphide, 228</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulphite, 120</td>
<td>hexafluoride, 214</td>
<td></td>
<td></td>
</tr>
<tr>
<td>telluride, 124</td>
<td>hydridioxide, 218</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tellurite, 124</td>
<td>hydroxol, 6, 210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetraborate, 134</td>
<td>monoxide, 219</td>
<td>hydrated, 219</td>
<td></td>
</tr>
<tr>
<td>tetracarbonyl, 131</td>
<td>nitrite, 232</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetrachlorplatinite, 287</td>
<td>octachloride, 215, 217</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetrasulphide, 120</td>
<td>octafluoride, 213</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetroxide, 118</td>
<td>oxides, 219</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thio-antimonite, 130</td>
<td>oxysulphide, 229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thio-carbonate hexammoniate, 133</td>
<td>sesquioxide, 219</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thiocyanate, 132</td>
<td>sulphite, 229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thio-orthophosphate, 129</td>
<td>tetrachloride, 215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thio-phosphophosphate, 129</td>
<td>tetrafluoride, 214</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thio-phosphophosphate, 129</td>
<td>tetra-iodide, 218</td>
<td></td>
<td></td>
</tr>
<tr>
<td>thiosulphate, 121</td>
<td>tetrasulphide, 229</td>
<td></td>
<td></td>
</tr>
<tr>
<td>triphosphide, 128</td>
<td>tetroxide, 221</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tungsten, 107</td>
<td>trichloride, 215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vanadate, 130</td>
<td><strong>Osmium, colloidal, 210</strong></td>
<td>comparison with iron and Ruthenium, 12</td>
<td></td>
</tr>
<tr>
<td>vitriol, 121</td>
<td></td>
<td>detection, 337</td>
<td></td>
</tr>
<tr>
<td>Nickelin, 106</td>
<td></td>
<td>estimation, 338</td>
<td></td>
</tr>
<tr>
<td>Nickeline, 78, 80, 129</td>
<td></td>
<td>history, 208</td>
<td></td>
</tr>
<tr>
<td>Nickelic fluoride, 111</td>
<td></td>
<td>occurrence, 208</td>
<td></td>
</tr>
<tr>
<td>sulphate, 123</td>
<td></td>
<td>physical constant, 5</td>
<td></td>
</tr>
<tr>
<td>Nickelonickel oxide, 117</td>
<td></td>
<td>properties, 200</td>
<td></td>
</tr>
<tr>
<td>selenide, 123</td>
<td></td>
<td>preparation, 208</td>
<td></td>
</tr>
<tr>
<td>Nickelous nickelite, 117</td>
<td></td>
<td>separation from platinum metals, 342–346</td>
<td></td>
</tr>
<tr>
<td>Nicomelane, 78, 80</td>
<td></td>
<td>table of compounds, 13</td>
<td></td>
</tr>
<tr>
<td>Nitrocoobalt, 59</td>
<td></td>
<td>uses, 212</td>
<td></td>
</tr>
<tr>
<td>Nitronickel, 126</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrosochlor-ruthenates, 150</td>
<td><strong>Osmium, colloidal, 210</strong></td>
<td>comparison with iron and ruthenium, 12</td>
<td></td>
</tr>
<tr>
<td>Nitrosyl bromplatinate, 309</td>
<td></td>
<td>detection, 337</td>
<td></td>
</tr>
<tr>
<td>Nitrosyl chlorplatinate, 309</td>
<td></td>
<td>estimation, 338</td>
<td></td>
</tr>
<tr>
<td>Nitrosyl hexammoniate, 133</td>
<td></td>
<td>history, 208</td>
<td></td>
</tr>
<tr>
<td>Osmic acid, 220</td>
<td></td>
<td>occurrence, 208</td>
<td></td>
</tr>
<tr>
<td>Osmic chlorides, 216</td>
<td></td>
<td>physical constant, 5</td>
<td></td>
</tr>
<tr>
<td>Osminitrites, 233</td>
<td></td>
<td>properties, 200</td>
<td></td>
</tr>
<tr>
<td>Osmiridium, 208</td>
<td></td>
<td>preparation, 208</td>
<td></td>
</tr>
<tr>
<td>analysis of, 340</td>
<td></td>
<td>separation from platinum metals, 342–346</td>
<td></td>
</tr>
<tr>
<td>Osmisulphites, 230</td>
<td></td>
<td>table of compounds, 13</td>
<td></td>
</tr>
<tr>
<td>Osmochlorides, 216</td>
<td></td>
<td>uses, 212</td>
<td></td>
</tr>
<tr>
<td>Osmocyanic acid, 225</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Osmocyanides, 225</td>
<td><strong>Osmium alloys, 212</strong></td>
<td>bromides, 217</td>
<td></td>
</tr>
<tr>
<td>Osmium. See Chap. VII</td>
<td>chlorides, 224</td>
<td>cyanide, 223</td>
<td></td>
</tr>
<tr>
<td>atomic weight, 3</td>
<td>comparison with iron and ruthenium, 12</td>
<td>diammine hydroxide, 231</td>
<td></td>
</tr>
<tr>
<td>catalytic activity, 182</td>
<td>detection, 337</td>
<td>dichloride, 214</td>
<td></td>
</tr>
<tr>
<td>chemical properties, 182</td>
<td>estimation, 338</td>
<td>dihydroxide, 219</td>
<td></td>
</tr>
<tr>
<td>colloidal, 6, 184</td>
<td>history, 208</td>
<td>di-oxide, 219</td>
<td></td>
</tr>
<tr>
<td>comparison with nickel and platinum, 16</td>
<td>separation from platinum metals, 342–346</td>
<td>hydrated, 219</td>
<td></td>
</tr>
<tr>
<td>crystalline, 184</td>
<td>table of compounds, 13</td>
<td>pyrophoric, 219</td>
<td></td>
</tr>
<tr>
<td>detection, 7, 334</td>
<td>uses, 212</td>
<td>colloidal, 220</td>
<td></td>
</tr>
<tr>
<td>estimation, 335</td>
<td></td>
<td>disulphide, 228</td>
<td></td>
</tr>
<tr>
<td>history, 174</td>
<td></td>
<td>hexafluoride, 214</td>
<td></td>
</tr>
<tr>
<td>occlusion of gases, 177</td>
<td></td>
<td>hydridioxide, 218</td>
<td></td>
</tr>
<tr>
<td>hydrogen, 178</td>
<td></td>
<td>hydroxol, 6, 210</td>
<td></td>
</tr>
<tr>
<td>occurrence, 174</td>
<td></td>
<td>monoxide, 219</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>hydrated, 219</td>
<td></td>
</tr>
</tbody>
</table>
Palladium, permeability, 176
physical constants, 5
physical properties, 175
preparation, 174
of pure, 175
separation from platinum metals, 342–345
spongy, 187
table of compounds, 17
uses, 188
volatilisation, 4, 5, 264
Palladium alloys, 192
amalgam, 194
antimonides, 206
black, 187
bromide, 198
chlorides, 195
cyanide, 206
dichloride, 195
di-oxyde, hydrated, 202
disulphide, 203
fluoride, 195
iodide, 200
monosilicide, 207
monosulphide, 203
monoxide, 201
nitrates, 205
nitrites, 205
oxides, 200
selenate, 204
selenide, 204
selenoxide, hydrated, 201
suboxide, 200
subselene, 204
subsilicide, 207
subsuphde, 203
sulphate, 204
sulphate, 204
thiocyanate, 206
trichloride, 197
Palladobromides, 199
Palladocyanides, 206
Palladonitrites, 205
Palladosalts. See Palladium
Passivity of cobalt, 7, 29
iron, 7
nickel, 7, 92
platinum, 268, 305
Pateroite, 58
Pentabrompalladates, 199
Pentabromrhodites, 144
Pentachlorobenzenes, 144
Pentachlorohydroxyplatinic acid, 296
Pentachloropalladate, 197
Pentachloroplatinous acid, 288
Pentachlororhodites, 163
Pentachlororuthenites, 141
Pentlandite, 78, 80, 82
Per-ruthenates, 147
Platinic salts. See Platinum
Platinicyanides, 326
Platinite, 103
Platinocyanides, 316–326
Platinoid, 106
Platinonitrites, 309
Platinous salts. See Platinum
Platinum. See Chap. IX

Platinum, atomic weight, 3, 275–278
catalytic activity, 267
crystallographic properties, 265
colloidal, 269
comparison with nickel and palladium, 16
crystalline, 6, 269
detection of, 7, 340
diffusion of gases, 264
determination, 341
explosive, 274
fulminating, 297
history, 265
native, 257
occurrence, 256
passivity, 268
physical constants, 5
properties, 262
preparation, 257
of pure, 261
refining of, 259
separation from platinum metals, 342–345
solubility of gases in, 265
table of compounds, 17
uses of, 278
volatility, 4, 5, 263
world production, 279
Platinum alloys, 280
amalgam, 284
antimonide, 313
black, 273
bromides, 297
carbonyl derivatives, 313–315
carbonyls, 285
chlorides, 285
cyanide, 302
cyanide, 315
di-antimoniode, 313
dibromide, 297
carbonyl, 314
dichloride, 285
diphosgene dicarbonyl, 314
monocarbonyl, 313
sesquicarbonyl, 313
dicyanide, 315
difluoride, 285
diiodide, 301
carbonyl, 314
di-oxyde, hydrated, 304
diphosphide, 312
disulphide, 306
ditelluride, 309
dithiocyanate, 206
d-feature from nickel matte, 261
dihydrosol, 6, 269
solid, 273
iodides, 301
monochloride, 285
carbonyl, 303
monoxide, 285
monochloride, 315
hydrated, 303
monophosphate, 312
monoselendic, 308
monosilicide, 299
monosulphide, 306
carbonyl, 315
monosulphide, 306
monotelluride, 309
<table>
<thead>
<tr>
<th>Platinum ores, 256</th>
</tr>
</thead>
<tbody>
<tr>
<td>analyses, 257, 258</td>
</tr>
<tr>
<td>oxides, 303</td>
</tr>
<tr>
<td>oxysulphide, 307</td>
</tr>
<tr>
<td>phosphides, 312</td>
</tr>
<tr>
<td>plating, 267</td>
</tr>
<tr>
<td>ruthenocyanide, 153</td>
</tr>
<tr>
<td>selenides, 308</td>
</tr>
<tr>
<td>sesquioxide, hydrated, 303</td>
</tr>
<tr>
<td>sesquisulphide, 306</td>
</tr>
<tr>
<td>silicides, 329</td>
</tr>
<tr>
<td>solder, 267</td>
</tr>
<tr>
<td>sponge, 274</td>
</tr>
<tr>
<td>stannate, 327</td>
</tr>
<tr>
<td>subphosphide, 312</td>
</tr>
<tr>
<td>subalicide, 329</td>
</tr>
<tr>
<td>substitutes, 279</td>
</tr>
<tr>
<td>subtelluride, 308</td>
</tr>
<tr>
<td>sulphate, 307</td>
</tr>
<tr>
<td>sulphides, 308</td>
</tr>
<tr>
<td>sulphite, 307</td>
</tr>
<tr>
<td>tellurides, 308</td>
</tr>
<tr>
<td>tetrabromide, 298</td>
</tr>
<tr>
<td>tetrachloride, 288</td>
</tr>
<tr>
<td>hydrates, 290</td>
</tr>
<tr>
<td>tetrafluoride, 285</td>
</tr>
<tr>
<td>tetra-iodide, 304</td>
</tr>
<tr>
<td>thiocarbonate, 315</td>
</tr>
<tr>
<td>thiocyanate, carbonyl, 315</td>
</tr>
<tr>
<td>thioestannates, 329</td>
</tr>
<tr>
<td>trichloride, 288</td>
</tr>
<tr>
<td>tricyanide, 326</td>
</tr>
<tr>
<td>tri-oxide, 305</td>
</tr>
<tr>
<td>triselenide, 308</td>
</tr>
</tbody>
</table>

Platinum metals, analysis of, qualitative, 342
quantitative, 344

Porcelain-painting, 33, 48, 49

Porpesite, 174

Potassium aquobromruthenate, 144
aquochlor-ruthenate, 143
barium osmocyanide, 234
platinocyanide, 324
bromiridate, 247
bromiridite, 247
bromosmate, 217
bromplladate, 199
bromplladite, 199
bromplladonitrite, 205
bromplatinate, 300
bromruthenate, 144
bromruthenite, 144
calcium platinocyanide, 321
chlor-iridate, 245
chlor-iridite, 243
chlorosmate, 216
chlorosmite, 215
chlorplladate, 198
chlorplladite, 196
chlorplladonitrite, 205
chlorplladinate, 294
chlor-ruthenate, 142
chlor-ruthenite, 141
cobalt alum, 56
carbonate, 67
cobaltite, 81

Potassium cobalt nitrite, 59
sulphate, 56
sulphite, 52
cobalticyanide, 69
cobaltinitrite, 60
cobalto-azoimide, 59
cobaltocyanide, 68
fluorosmate, 214
hexachlor-rhodite, 162
iodiridate, 247
iodiridite, 247
iodopalladite, 200
iodopalladonitrite, 205
iodoplattinate, 302
iodosmate, 218
iridicyanide, 254
iridinitrite, 253
iridium alum, 251
chlor-nitrite, 253
sulphite, 250
lithium platinocyanide, 324
nickel azoimide, 125
chromate, 125
nitrite, 126
selenate, 124
sulphate, 123
nitrosochromosmate, 232
nitrosochlorosmate, 232
nitrosochlor-ruthenate, 150
nitroso-iodosmate, 232
osmate, 220
osmiamate, 232
osninitrite, 233
osmopyanide, 233
osmyl bromide, 225
chloride, 224
nitrite, 225
oxynchloride, 227
oxyninitrite, 228
palladocyanide, 206
palladothioyanate, 206
pentabromrhodite, 164
pentachlor-rhodite, 163
per-ruthenate, 148
platinocyanide, 327
platinocyanide, 323
platinonitrite, 310
rhodicyanide, 173
rhodinitrite, 170
rhodium alum, 170
ruthenate, 147
ruthenium nitrite, 151
nitrosoclorhloride, 150
ruthenocyanide, 151
selenocyanoplattinate, 328
sodium platinocyanide, 325
strontium platinocyanide, 325
tetabrompllatinete, 298
tetrachloridobromplatinete, 303
tetrachlorplatinete, 287
thiocyanoplattinate, 328
thiocyanoplattinate, 327
hexachlor-rohodite, 162
thiopalladite, 203
thiopladin, 307

Pyromelane, 78, 80
Rhodium. See Chap. V
atomic weight, 157-159
colloidal, 156
comparison with cobalt, 14
iridium, 14
detection, 7, 333
estimation, 334
explosive, 156
history, 154
occurrence, 154
physical constants, 5
properties, 155
preparation, 154
separation from platinum metals, 342-345
table of compounds, 15
uses, 157
volatilisation, 5, 155
Rhodium alloys, 159
alums, 169
black, 157
ammonium chloronitrate, 171
cyanide, 173
dichloride, 159
dioxide, 166
hydrated, 166
double sulphides, 169
gold, 154
hydrogen sulphide, 168
monosulphide, 167
nitrate, 171
nitrite, 170
potassium nitrite, 170
sesquioxide, 165
hydrated, 166
sesquisulphide, 167
sodium sulphate, 169
sulphate, 169
basic, 169
sulphite, 169
sulphhydrate, 168
tribromide, 164
dichloride, insoluble, 160
soluble, 161
di-iodide, 165
di-oxyde, 167
uranyle nitrate, 171
Rhodobromides, 164
Rhodochlorides, 164
Rinman’s Green, 48
Rubidium brompalladate, 200
brompalladate, 199
bromplatinate, 200
bromiruthenate, 144
bromiruthenite, 144
chlor-iridate, 246
chlor-iridite, 244
chlorosmate, 216
chloropalladate, 198
chloropalladite, 197
chlorplatinate, 294
Rubidium chlorplatinate, 287
chlor-ruthenate, 143
cobalt alum, 56
iridium alum, 252
nickel chloride, 112
chromate, 125
selenate, 124
sulphate, 123
nitrosoclor-ruthenate, 150
pentabromrhodite, 165
pentachlorpalladate, 197
pentachlor-rhodite, 164
platinocyanide, 324
platanonitrite, 310
rhodium alum, 170
Rubenates, 147
per-, 147
Ruthenichlorides, 142
Ruthenites, 146
Ruthenechlorides, 141
Ruthenium. See Chap. IV
atomic weight, 139-140
chemical properties, 138
colloidal, 138
comparison with iron and osmium, 12
crystalline, 137
detection, 330
estimation, 333
explosive, 138
history, 136
occlusion of gases, 137
occurrence, 136
physical constants, 5
properties, 137
preparation, 136
of pure, 137
separation from platinum metals, 342-345
spongy, 138
tables of compounds, 13
volatilisation, 5, 264
Ruthenium alloys, 140
dicarbonyl, 151
dichloride, 140
di-oxyde, 149
disulphide, 148
dithionate, 149
fluoride, 140
nitrites, double, 151
nitrosocloride, 149
nitrosotrihydroxide, 149
nitrosotribromide, 150
nitrosotri-iodide, 150
oxides, table of, 145
oxychlorides, 143
peroxide, 146
phosphides, 151
sesquioxide, 145
hydrated, 145
sesquisulphide, 148
sesquisulphite, 148
silicide, 153
sponge, 138
sulphate, 149
tetrahydroxide, 142
tetroxide, 146
Ruthenium tribromide, 143
trichloride, 141
tri-iodide, 144
trisulphide, 148

Safflowerite, 19, 20, 65
Safflower, 73
Savelsberg Process, 89
Selenpalladium, 174
Sessincarbonyl platinum dichloride, 313
Silver bromosmate, 218
bromplatinate, 300
chlor-iridate, 246
chlor-iridite, 244
chlor-osmate, 216
chloroplatisate, 294
cobalticyanide, 71
cobaltitrintrite, 62
iridicyanide, 255
osmiane, 232
osmintrite, 233
oxymyloxytritrite, 228
palladonitrte, 205
pentachlorhydroxyplatinate, 296
platincyanide, 327
platinonitrte, 310
ruthenate, 147
ruthenocyanide, 152
tetrahromdihydroxyplatinate, 300
tetrahromdihydroxyplatinate, 296
tetra-ido-dihydroxyplatinate, 302
thiocyanoplatinate, 328
thiocyanoplatinites, 327

Sierskite, 235
Smalt, 73
Smaltite, 19, 20, 65, 79
Sodium bromiridate, 247
bromiridate, 247
bromosmate, 217
bromoplatisate, 199
bromoplatisate, 300
chlor-iridate, 245
chlor-iridite, 244
chlorosmate, 216
chloroplatisate, 197
chloroplatisate, 295
cobalticyanide, 71
cobaltitrintrite, 60
red, 61
hexachlor-rhodite, 182
iodiridate, 247
iodiridate, 247
iodoplatisate, 302
iridintrite, 253
iridium chloronitrte, 253
sulphite, 251
osmate, 220
osmiamente, 232
osmintrite, 233
osmium hexachloride, 217
oxymoxygenitrte, 228
palladocyanide, 206

Sodium palladosulphite, 204
pentabromrhodite, 165
per-ruthenate, 148
platinocyamine, 327
platinocyamine, 325
platinonitrte, 310
potassium cobaltinitrite, 61
platinocyamine, 325
rhodate, 187
rhodinitrite, 151
rhodium sulphate, 160
ruthenate, 147
ruthenium nitrite, 161
tetrahromdihydroxyplatinate, 300
tetrahromplatinite, 287
thiocyanoplatinate, 328
thiopalladate, 204
thiopalladates, 307
Sperryrite, 257, 312
Stainless cutlery, 36
Stellite, 36
Strontium bromoplatisate, 199
bromoplatisate, 300
chloroplatisate, 296
cobaltinitrite, 62
osmintrite, 233
osmintrite, 233
osmyloxytritrite, 228
palladonitrte, 205
pentachlorhydroxyplatinate, 296
platincyanide, 325
platinonitrte, 311
potassium platinocyamine, 325
ruthenate, 147
ruthenocyanide, 152
tetrahromdihydroxyplatinate, 300
thiocyanoplatinate, 328
thiocyanoplatinites, 327
Sudbury ore, origin of, 82
Syepoorite, 20, 51
Sympathetic inks, 34, 42

Temiskamite, 78, 80
Tetrabromdihydroxyplatinic acid, 300
Tetrabromoplatisates, 199
Tetrabromplatinates, 298
Tetrachlorhydroxyplatinic acid, 296
Tetrachlorplattinates, 196
Tetrachlorplatinates, 286
Tetrachlorplatinous acid, 285
Tetracobalt triphosphide, 64
Tetra-ido-dihydroxyplatinic acid, 302
Tetrancikel silicade, 133
suboxide, 115
Tetranitro-platinates, 309
Tetranitro-platinous acid, 309
Texasite, 78, 80
Thallium chloroplatisate, 295
chlor-iridate, 246
chlor-iridite, 244
iridium alum, 252
pentachlorhydroxyplatinate, 296
rhodium alum, 170
tetrahromdihydroxyplatinate, 300
tetrahromplatinite, 287
tetra-ido-dihydroxyplatinate, 302
Thenard's blue, 48
Thiocyanoplatinates, 328
Thiocyanoplatinites, 327
Thiopalladites, 203
Thioplatmates, 307
Tin chlorplatinate, 295
  ruthenocyanide, 153
Transitional elements, 2
Triads, 1
Trichlorhydroxyplatinites, 288
Trichlorhydroxyplatinous acid, 287
Tricobalt di-arsenide, 65
  diphosphide, 64
  tetrasulphide, 52
  tetroxide, 49
Trinicobalt di-arsenide, 129
  suboxide, 115
  tetrasulphide, 120
  tetroxide, 117
Triplatinum tetroxide, 303
Tri-rhodium tetroxide, 165
Tungsten nickel, 107
Turquoise green, 49

ULLMANTITE, 79, 80
Uranyl platinocyanide, 325

VIVIANITE, 65

WAD, 19, 20
Whartonite, 78, 80
White nickel, 78
Willyamite, 19
Wöhler’s Method, 20
Wolfachite, 79, 80
ZAFFRE, 65, 73
Zaratite, 80
Zinc brompalladite, 199
  bromplatinate, 300
  chlorpalladate, 198
  chlorpalladite, 197
  chlorplatinate, 295
  cobaltinitrite, 62
  cobaltocyanide, 68
  iodoplatinate, 302
  osminitrite, 233
  platinocyanide, 325
  platinonitrile, 311
  ruthenocyanide, 152
  tetrachlorihydroxyplatinate, 296
  tetrachlorplatinite, 287
Zirconyl chlorplatinate, 295
  tetrachlorplatinite, 287