CHEMISTRY OF THE RARER ELEMENTS

BY

B. SMITH HOPKINS
PROFESSOR OF INORGANIC CHEMISTRY
UNIVERSITY OF ILLINOIS

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PREFACE

THE term "rare elements" is conveniently applied to those members of the Periodic Table whose chemistry is little known. Some of these elements are so scarce that their study has of necessity been difficult; others are abundant in nature, but their development has been retarded by lack of sufficient interest; still others have only recently been discovered, and sufficient time has not yet elapsed for them to lose the interest inherent in newness. The "rare elements" then should be understood to include those elements which are little known either because of scarcity, neglect, or ignorance. The chemistry of some of these elements is developing rapidly, since we are just beginning to appreciate something of their interest and usefulness. Rapid advancement has followed such an awakening, and the names of some such substances have become household words. In other cases interest has been less keen and advancement has been slow.

The purpose of this work is to call attention both to the advances which have recently been made in our knowledge of the so-called "rare" elements and also to the need of further research in the development of many of the less familiar elements. This book is the outgrowth of a lecture course given for many years at the University of Illinois, first by Dr. Clarence W. Balke, and later by the author. This course has been essentially a study of the Periodic Table with special reference to the elements which are treated very briefly or entirely ignored in most textbooks on Inorganic Chemistry. For the present course a working knowledge of the common elements is understood, and they are mentioned briefly for the purpose of showing the relationship between the rare elements and their more familiar neighbors.

The chemistry of many of the rare elements is still in a decidedly chaotic state. The literature contains conflicting statements, misleading discussions, and downright errors. In such cases the author has attempted to select those statements which seem to bear the greater weight of authority. Where differences of opinion exist for the settling of which more information is needed, an attempt has been made to present an impartial summary. Care has been exercised to eliminate as far as possible inaccurate, misleading, and untrue statements. It is too much, however, to expect that a book of this sort can be made free from errors either direct or implied. The author will be glad to have his attention called to any undetected errors, for which he alone must be held responsible. Suggestions will also be gladly received.

In a course which has been developed by a process of this sort many of the original sources of information have been lost. The writer would be glad to acknowledge his indebtedness to every author from whom information has been received, but this is manifestly impossible, since the material has been collected from a very wide range of sources and over a period of several years. Much material has been gleaned from such standard works as: Abegg, *Handbuch der anorganischen Chemie;* Browning, *Introduction to the Rarer Elements;* Friend, *Text-book of Inorganic Chemistry;* Gmelin-Kraut, *Handbuch der anorganischen Chemie;* Johnstone, *Rare Earth Industry;* Levy, *Rare Earths;* Mellor, *Modern Inorganic Chemistry;* Roscoe and Schlorlemmer, *Treatise on Chemistry;* Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements;* Spencer, *Metals of the Rare Earths;* Stewart, *Recent Advances in Inorganic and Physical Chemistry;* Venable, *Zirconium;* and many others. Constant use has also been made of the current scientific journals. An attempt has been made to give sufficient references to the literature to permit the student who is interested in any particular phase of the discussion to pursue his investigation farther. These references also serve the double purpose of giving the authority upon which certain statements are made and of acknowledging the author's indebtedness for the information given.

The author is especially indebted to the following persons who have read portions of the manuscript and offered many helpful suggestions for its improvement, or have contributed in various ways in the compilation of the material: C. W. Balke, H. G. Deming, Saul Dushman, E. A. Engle, W. D. Engle, W. D. Harkins, Maude C. Hopkins, H. C. Kremers, Victor Lenher,

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If this book serves to create greater interest in those elements which are usually slighted in the study of Inorganic Chemistry, the author will feel amply repaid for the work which has been necessary in the assembling and editing of the material herewith presented.

B. S. HOPKINS

URBANA, ILLINOIS,
August 1, 1923.

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CHAPTER I

THE PERIODIC SYSTEM

Historical. — Between 1802 and 1808 occurred the historic controversy between Proust and Berthollet[1] concerning the Law of Fixed Ratios. This discussion ended with Proust convincing chemists that chemical compounds possess a definite composition. In 1808 John Dalton published[2] a connected account of his Atomic Theory, upon which modern chemistry is based. In this way the theory of elements came to be accepted among scientific men, and very quickly efforts were made to find a fundamental relationship between various elemental forms of matter.

In 1815 Prout called attention[3] to the fact that when the atomic weights of the elements were expressed upon the hydrogen basis, the values of the other elements were very close to whole numbers, and expressed the opinion that hydrogen was the primary element from condensations of which resulted all of the other so-called elements. Prout's Hypothesis was received enthusiastically by some and ridiculed by others. The discussion concerning this theory has occupied the minds of scientific men of all nations for a large part of the nineteenth century and in a modified form has continued down to the present time.

Thomas Thomson, in England, was an enthusiastic follower of Prout who tried to show experimentally[4] that the Hypothesis was true. His results were questioned especially by Berzelius, in Sweden, whose revised table of atomic weights, published in

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[1] See Miss Freund, *The Study of Chemical Composition*, Cambridge University Press, 1904, chapter v, and Hartog, *Nature*, **50** 149 (1894).

[2] *A New System of Chemical Philosophy*, 2 vols., 1807 10.

[3] *Ann. Phil.* **11** 321 (1815), and **12** 111 (1816).

[4] *An Attempt to Establish the First Principles of Chemistry by Experiment*, London, 1825.

1825, contained values which differed widely from Thomson's. Gmelin, in Germany, was inclined to accept the Hypothesis, and Dumas, in France, was outspoken in its support, especially after his work [1] upon the atomic weight of carbon showed that the ratio between carbon and hydrogen was almost exactly 12 to 1. The accurate determination of the atomic weight of chlorine [2] by Marignac, in France, showed its value to be almost exactly 35.5. This led Marignac in 1844 to propose that the Prout unit be half the atomic weight of hydrogen. Dumas welcomed this suggestion, but his own work [3] later led him to suggest the adoption of $\frac{1}{4}$ the hydrogen atom as the ultimate unit. In 1860 the classic atomic weight work of Marignac and Stas gave values showing variations altogether too large to be accounted for by experimental error and made further subdivisions of the "unit" necessary. So the Hypothesis lost standing owing to the necessity of frequent revision of the ultimate unit.

In 1880 interest in the idea was revived by Mallet [4] whose work upon the atomic weight of aluminium showed that it belonged to the long list of elements whose equivalents are approximately whole numbers. Mallet called attention to the fact that 10 of the 18 elements whose atomic weights were best known had atomic weights differing from whole numbers by less than $\frac{1}{10}$ of a unit. He suggested that possibly certain constant errors might have influenced the accepted values of certain elements. A more recent revival of interest in Prout's Hypothesis was produced by Strutt, who called attention [5] to the fact that of the elements whose atomic weights are most accurately known, 12 have values which are almost exactly whole numbers. This is a far larger number than can be accounted for by the law of probability, so that "we have stronger reasons for believing in the truth of Prout's Law than in that of many historical events which are universally accepted as unquestionable." Along the same line Harkins has pointed out [6] that the atomic weights of 17 of the first 21 elements show an average deviation from whole numbers of 0.05 and argues that such a situation cannot be explained on the basis of chance.

[1] Dumas and Stas, *Ann. chim. phys.* **3** (III) 5 (1841).

[2] *Compt. rend.* **14** 570 (1842).

[3] *Ann. chim. phys.* **3** 55, 129 (1859).

[4] *Am. Chem. Jour.* **3** 95 (1880).

[5] *Phil. Mag.* **6** (i) 311 (1901).

[6] *Jour. Am. Chem. Soc.* **37** 1370 (1915).

The theory that the elements are in reality a series of condensation products of some primal element which must resemble the protyle of the ancient philosophers has been a fascinating theory from the beginning. It has been repeatedly denounced as an illusion, but nevertheless it has continued to claim periodic attention among scientists. In the light of modern theories of atomic structure, it is not strange that the Hypothesis of Prout should reappear in modified form. Harkins and Wilson have shown [1] that at least the lighter elements may be considered as composed of a certain number of atoms of hydrogen and helium. This theory finds striking confirmation in the study of the radioactive elements and from the experiments of Rutherford, who has found evidence [2] for the conclusion that nitrogen atoms may be disrupted by bombardment with alpha particles, with the liberation of hydrogen.

That the elements possessed relationships of a different sort was shown soon after the establishment of Dalton's Atomic Theory. As early as 1817, Doebereiner called attention to the fact that strontium had an atomic weight which was very close to the mean of the values for calcium and barium, while these three elements showed close similarity in both physical and chemical properties. Later he also showed that there are other triads in which the same general relationship exists, such as:

	Atomic Weights	Mean
Calcium	40.07	
Strontium	87.63	88.72
Barium	137.37	
Chlorine	35.46	
Bromine	79.92	81.19
Iodine	126.92	
Sulfur	32.06	
Selenium	79.2	79.78
Tellurium	127.5	

The Triads of Doebereiner apparently created very little interest, for it was not until 1850 that Pettenkofer took the next step when he expressed the belief that the differences

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[1] *Jour. Am. Chem. Soc.* **37** 1367, 1383 (1915).

[2] E. E. Rutherford, *Phil. Mag.* **37** 581 (1919).

between the atomic weights of the members of a "natural group" were multiples of a constant number, thus:

	Atomic Weights	Differences		Atomic Weights	Differences
Lithium . .	7		Oxygen . .	16	
		16			16
Sodium . .	23		Sulfur . .	32	
		16			3×16
Potassium .	39		Selenium .	80	
					3×16
			Tellurium .	127.5	

In 1853 Gladstone arranged[1] the elements in the order of increasing atomic weights, but so many of the values accepted at that time were faulty that no broad generalization was possible.

In the following year J. P. Cooke discussed[2] "the numerical relations between the atomic weights with some thoughts on the classification of the chemical elements." He pointed out that Doebereiner's Triads actually broke up natural groups of elements, as, for example, the halogen group which contains four closely related elements. He proposed a classification by which the elements were divided into series, similar to the homologues of Organic Chemistry. He took into consideration the general chemical analogies of the elements, the types and relations of their compounds, and the crystallographic relations as well as the physical and chemical properties. Cooke's classification is generally regarded as the first effort to arrange the elements in groups by means of a comparative study of all the available chemical facts.

In 1857 Odling arranged[3] the elements in accordance with the "totality of their characters" and found 13 triads some of which were double and some incomplete. In each case the intermediate term "is possessed of intermediate properties and has an exactly intermediate atomic weight."

Two years later Dumas wrote[4] as follows: "When one arranges in the same series the equivalents (atomic weights) of the radicals of the same family whether in mineral or organic

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[1] *Phil. Mag.* **5** (iv) 313 (1853).

[2] Silliman's *Am. Jour. Sci.* **17** (ii) 387 (1854).

[3] *Phil. Mag.* **13** (ii) 423, and 480 (1857).

[4] *Ann. chim. phys.* **55** (iii) 209 (1859).

chemistry, the first term determines the chemical character of all the bodies which belong to the series. The type of fluorine reappears in chlorine, bromine, and iodine; that of oxygen in sulfur, selenium and tellurium; that of nitrogen in phosphorus, arsenic and antimony; that of titanium in tin; that of molybdenum in tungsten, etc."

These early attempts to classify the elements are interesting, but no attempt was made to include all the then known elements because of the lack of a consistent system of atomic weights. This essential was supplied in 1858 by the splendid work of Cannizzaro who was the first to utilize Avogadro's Hypothesis as the basis for atomic weight determinations. As a result of these revised atomic weights, order began to displace chaos and in 1862–63 appeared the first real attempt to include all the elements in a single classification. This work was done by A. E. B. de Chancourtois[1] who is generally given credit for first suggesting the relationships which may fairly be considered the forerunner of the periodic system. He arranged the elements spirally in the order of increasing atomic weights and divided the cylindrical helix into 16 vertical sections. Elements falling in the same vertical section had similar physical and chemical properties. This arrangement became known as the Telluric Screw and is recognized as embodying the fundamental idea of the periodic system, although the conception is hazy, the expression obscure, and the accompanying speculations misleading.

The next step was taken when John A. R. Newlands published a series of articles[2] in which attention was directed to the fact that when the elements are arranged in the order of atomic weight, the eighth element resembles the first. On account of the resemblance to the musical scale this generalization was known as the Law of Octaves. An examination of Newlands' table shows some inconsistencies, due at least in part to his failure to leave spaces for undiscovered elements. There is much to admire in Newlands' contribution, in spite of his inability to provide satisfactorily for the elements of higher atomic weight.

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[1] *Compt. rend.* **54** 757, 840, 967 (1862); **55** 600 (1862); **56** 253, 479 (1863); **63** 24 (1866). See also P. J. Hartog's article on "A Foreshadowing of the Periodic Law," *Nature*, **41** 186 (1889).

[2] *Chem. News*, **7** 70 (1863); **10** 11, 59, 94 (1864); **12** 83, 94 (1865); **13** 113, 130 (1866).

Thus, it is seen that the idea of a fundamental relationship between the elements had been growing gradually for a half century from the isolated Triads of Doebreiner to the Octaves of Newlands and the Table of de Chancourtois. It is no wonder that, with these preliminary steps, two men should announce a periodic arrangement almost simultaneously and doubtless quite independently.

TABLE I

Newlands' Law of Octaves

H	F	Cl	Co, Ni	Br	Pd	I	Pt, Ir
Li	Na	K	Cu	Rb	Ag	Cs	Tl
Gl	Mg	Ca	Zn	Sr	Cd	Ba, V	Pb
B	Al	Cr	Y	Ce, La	U	Ta	Th
C	Si	Ti	In	Zr	Sn	W	Hg
N	P	Mn	As	Di, Mo	Sb	Nb	Bi
O	S	Fe	Se	Ro, Ru	Te	Au	Os

Lothar Meyer published *Die Modernen Theorien der Chemie* in 1864, in which appeared a table containing most of the then known elements and leaving spaces for undiscovered elements. Those elements which appear in the same column have similar properties, but the system was not complete, and was little more than that of Newlands.

In 1869–71 Mendeléeff published[1] an arrangement of the elements in the order of increasing atomic weight in which it was shown clearly that there is a periodic recurrence of properties. In 1870 Meyer published a paper[2] giving a table almost identical with Mendeleeff's and stating that "the properties of the elements are, for the most part, periodic functions of their atomic weights." Later he modified his table slightly and suggested a spiral arrangement, which has the advantage of showing both the continuous nature of the scheme, and the periodic recurrence of certain properties.

While both Meyer and Mendeléeff deserve great credit for the part each played in the clearing up of the periodic relationship, it is quite clear that neither one deserves all the credit for this useful generalization. The verdict of the chemical world

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[1] *J. Russ. Chem. Soc.* **1** 60 (1869); **2** 14 (1870); **4** 25, 348 (1871).

[2] *Annalen Suppl.* **7** 354 (1870).

TABLE II

Mendeléeff's Table[1] *(1871)*

	I	II	III	IV	V	VI	VII	VIII
	— R_2O	— RO	— R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	— RO_4
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59 Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	Y = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104 Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	Di = 138	Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	Er = 178	La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197 Pt = 198, Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

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[1] *Annalen Suppl.* **8** 151 (1872).

TABLE III

Comparison of Eka-silicon with Germanium

	EKA-SILICON (PREDICTED, 1871)	GERMANIUM (DISCOVERED, 1886)
Atomic weight	72	72.3
Specific gravity	5.5	5.47
Atomic volume	13.	13.2
Color	Dirty gray	Grayish-white
Calcination produces	EsO_2, white powder	GeO_2, white powder
Effect of H_2O	Will decompose steam with difficulty	Does not decompose water
Effect of acids	Slight effect	Not attacked by HCl but soluble in aqua regia, oxidized by HNO_3
Effect of alkalies	No pronounced action	Solution of KOH has no effect; oxidized by fused KOH
Production of the element	EsO_2 and EsK_2F_6 reduced by sodium	GeO_2 reduced by C and GeK_2F_6 by Na
Properties of the oxide	Refractory; specific gravity 4.7; less basic than TiO_2 or SnO_2; more basic than SiO_2	Refractory; specific gravity 4.703; feebly basic
Properties of the chloride	$EsCl_4$ will be a liquid with boiling point under 100° and specific gravity 1.9 at 0°	$GeCl_4$ boils at 86° and has specific gravity 1.887 at 18°
Properties of the fluoride	EsF_4 will not be gaseous	GeF_4 is a solid
Organo-metallic compound	$Es(C_2H_5)_4$ boils at 160° and has specific gravity 0.96	$Ge(C_2H_5)_4$ boils at 160° and has specific gravity a little less than 1

gives greatest credit to Mendeléeff in spite of the fact that Meyer has some very ardent supporters. Oswald in his *Klassiker der exakten Wissenschaften*, No. 68, sets forth strong claims for the priority of Meyer's work, but one of the main reasons why Mendeléeff is given greater credit is because he ventured to predict the properties of certain unknown elements. He foretold the properties of the elements eka-boron (scandium), eka-silicon (germanium), and eka-aluminium (gallium). That he had a wonderfully clear conception of the meaning of his periodic table is shown by a comparison of the properties predicted for eka-silicon in 1871 with the properties of the element germanium discovered in 1886. (See Table III.) The predictions of the properties of eka-aluminium and eka-boron are equally striking. This remarkable achievement centered attention upon the Mendeléeff table and by some is considered an absolute proof of the truth of the theory. C. Winkler said: "It would be impossible to imagine a more striking *proof* of the doctrine of periodicity of the elements than that afforded by this embodiment of the hitherto hypothetical eka-silicon."

On the other hand, G. Wyruboff as late as 1896 considered the periodic system as "a very interesting and highly ingenious table of the analogies and dissimilarities of the . . . elements" and proposed to reject the whole generalization because of its defects, reasoning that "since the laws of nature admit of no exception, the periodic law must be considered as a law of nature definitely established which must be accepted or rejected as a whole." In spite of the bitter attacks made upon the system by those who claim that it has done more harm than good, the fact remains that it is a convenient basis for the classification of an endless array of facts. In addition it has been a vast benefit to the science of chemistry by reason of its stimulation to research.

Usefulness. — Mendeléeff pointed out four definite methods of using the periodic law:

1. As a means of classification it serves to systematize the details of chemistry and permits the student to group together a large number of facts, which would otherwise be in a disconnected and chaotic state. Not only are the chemical properties of the elements periodic functions of the atomic weight but there is also a periodic relationship in valence, specific gravity, atomic volume, melting point, boiling point, hardness, malleability, ductility, compressibility, coefficient of expansion, thermal conductivity, atent heat of fusion, heat of chemical combination, refractive index, color, distribution in nature, electrical conductivity, and magnetic susceptibility. The analogous compounds of the elements frequently show periodicity in uch properties as molecular volumes, melting points, boiling points, tability, and color. The specific heats of the elements furnish an exception o the rule since they are not periodic.

2. It offers a method of determining atomic weights of elements whose quivalents or combining weights are known. In this way beryllium,

indium, uranium, and certain of the rare earths were located in the positions which they now occupy.

3. The prediction of the properties of undiscovered elements was possible from a study of the properties of the adjacent known elements. In addition to predicting the discovery of scandium, gallium, and germanium, Mendeléeff predicted the discovery of ekacaesium, dwicaesium, ekaniobium, ekatantalum, dwi-tellurium, ekamanganese, and dwimanganese. The prediction of the Zero Group was obviously impossible before the discovery of any member of this family. But after the discovery and placing of helium and argon, the existence of other inert gases was to be expected, and undoubtedly the discovery of neon, krypton, and xenon was materially hastened by the fact that the periodic system indicated that such gases should exist.

4. The correction of faulty atomic weights is suggested whenever an element falls out of place or produces a "misfit" in the system. Thus, in 1870, the last triad in Group VIII brought platinum under iron and ruthenium and placed osmium under nickel and palladium. These relationships are obviously strained, and correction of the atomic weights of platinum, iridium, and osmium has removed this discrepancy. The atomic weights were:

	PLATINUM	IRIDIUM	OSMIUM
In 1870	195.7	196.7	198.6
In 1922	195.2	193.1	190.9

Defects. — The tables of Mendeléeff and Meyer contained several weak spots, some of which have not yet been satisfactorily strengthened. These defects may be briefly enumerated as follows:

1. The position of hydrogen is a puzzle. It is univalent and electropositive, so it is generally placed in Group I with the alkali metals. But it is certainly not a metal, since even in the solid form it is typically nonmetallic; it is easily displaced from organic compounds by the halogens and forms metallic hydrides which are in no way similar to the metallic alloys but bear a certain resemblance to the halogen salts.[1] So there is reason for placing it in Group VII near the gaseous non-metals. But a study of the chemical behavior of hydrogen shows that, like the metals, it forms its most stable compounds with the nonmetallic elements. Consequently the relationship of hydrogen to the other elements is still very much of an enigma.

2. The rare earth group furnishes another difficulty, since here we have a considerable number of elements differing from one another in atomic weight but possessing very similar properties. Several methods of disposing of the rare earths have been proposed, but they are not wholly satisfactory. (See chapter on Rare Earths.)

3. If the order of arrangements follows the atomic weights rigidly, certain elements fall out of place. Thus the positions of argon and potas-

[1] D. C. Bardwell, *Jour. Am. Chem. Soc.* **44** 2499 (1922).

sium, of cobalt and nickel, and of tellurium and iodine would be reversed, while their properties require the positions usually given them. This difficulty has disappeared since the introduction of atomic numbers as the basis of classification in place of the atomic weights used by Mendeleeff.

4. The symmetry of the system is destroyed by Group VIII, which contains triads in alternate series. These triads show a disturbing variation in valence. They show a certain transition of properties between the last members of the odd series and the first members of the following even series. Yet their presence is more puzzling than helpful.

5. The most serious defect in the system, especially in its usefulness in the laboratory, is that similar elements are sometimes in remote positions, while dissimilar elements are brought close together. These difficulties are most pronounced in qualitative analysis, in which the solubilities of salts are of prime importance. As illustrations of this defect it may be observed that copper and mercury, silver and thallium, barium and lead, have many similar properties which are not suggested by their positions in the table. On the other hand we might expect gold and caesium, rubidium and silver, and manganese and chlorine to resemble each other much more closely than they do. It is obvious, however, that no table could possibly show all the resemblances and contrasts of each element, and a detailed study of each of these elements justifies in a measure its usual position in the table.

Modern Arrangements of the Periodic Table. — The recognized advantages and weaknesses in Mendeléeff's table have produced a vast amount of discussion. The system has been bitterly attacked and earnestly defended, with apologies for its imperfections and suggestions for its improvement. As a result of this discussion progress has been made, but the problem is a complex one and much remains yet to be accomplished. It is evident that we cannot understand clearly the relationship which exists between the elements until we have a pretty clear conception of what an element is and know something of the structure of atoms. Recently great advances have been made in these directions, and any modern arrangement of the periodic table must be in strict harmony with our best information concerning atomic structure, must conform with the revelations of X-ray analysis, and must agree with the conclusions of studies in radioactivity. Accordingly in the recently suggested plans the elements are arranged in the order of atomic numbers, which removes the misfits found at the positions of argon and potassium, cobalt and nickel, and tellurium and iodine. Most of the modern arrangements also provide for the suitable placing of the isotopes, especially of the radioactive elements. The

TABLE IV

Werner's Periodic Table

—																															—	—
H 1.008																															—	He 4
Li 7.03																									Be 9.1	B 11	C 12	N 14.01	O 16.00	Fl 19	Ne 20
Na 23.05																									Mg 24.36	Al 27.1	Si 28.4	P 31.0	S 32.06	Cl 35.45	A 39.9
K 39.15	Ca 40.1																Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 55.9	Co 59.0	Ni 58.7	Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75.0	Se 79.1	Br 79.96	Kr 81.12
Rb 85.4	Sr 87.6																Y 89.0	Zr 90.6	Nb 94	Mo 96.0	—	Ru 101.7	Rh 103.0	Pd 106.5	Ag 107.93	Cd 112.4	In 115	Sn 119.0	Sb 120	Te 127.6	I 126.85	Xe 128
Cs 133	Ba 137.4	La 138	Ce 140	Nd 143.6	Pr 140.5	-	—	Sa 150.3	Eu 151.79	Gd 156	Tb 160	Ho 162	Er 166	-	Tu 171	Yb 173.0	—	—	Ta 183	W 184.0		Os 191	Ir 193.0	Pt 194.8	Au 197.2	Hg 200.0	Tl 204.1	Pb 206.9	Bi 208.5		—	
—	Ra 225		Th 232.5	—	—	—	—	—	—	—	—	—	—	—		—	—	—	—	U 238.5	—				—	—					—	

greatest difficulties still remaining in preparing a thoroughly satisfactory table are two in number: first, in showing the relationship of hydrogen to the other elements of the table; and, second, in making adequate provision for the rare earth group.

Modern arrangements of the table may be considered in two classes, those using a flat surface and those using three dimensions. Only the more important suggestions in each class can be considered here.

In order to provide space for the rare earth group, Werner has proposed[1] an arrangement shown in Table IV. This plan makes provision for all the elements, but it is cumbersome and lacks the simplicity and regularity of the Mendeleeff table, since as the sequence moves to the right across the page a uniform change of properties does not follow. The arrangement of Deming, Table V, brings out nicely the peculiar relationship which hydrogen bears to the rest of the elements and provides space for all the elements, the rare earth group taking a place in which we should expect to find only one or two single elements. This plan brings out some interesting relationships, but is complicated and does not show the isotopes of the radioactive elements. The table suggested by Dushman,[2] Table VI, has the advantage of simplicity and completeness. It shows the body of the rare earth group as an enlargement of the position which we would expect to be occupied by a single element in Group III and provides space for the isotopes of the radioactive elements.

Of the helical arrangements those by Soddy and Harkins are notable. In the former[3] the elements are arranged in the order of increasing atomic numbers around two helical cores, one of which has a sharpened end to signify the abrupt changes which take place when we pass through the Zero Group, while the other has a flattened end upon which is arranged the triads of Group VIII. The rare earth group is arranged in order along the surface of the helix in the position occupied by Group III. A flat surface drawing of Soddy's arrangement is shown in Fig. 1, but a small model in three dimensions brings out the relationships much more clearly. Harkins[4] uses two cylinders,

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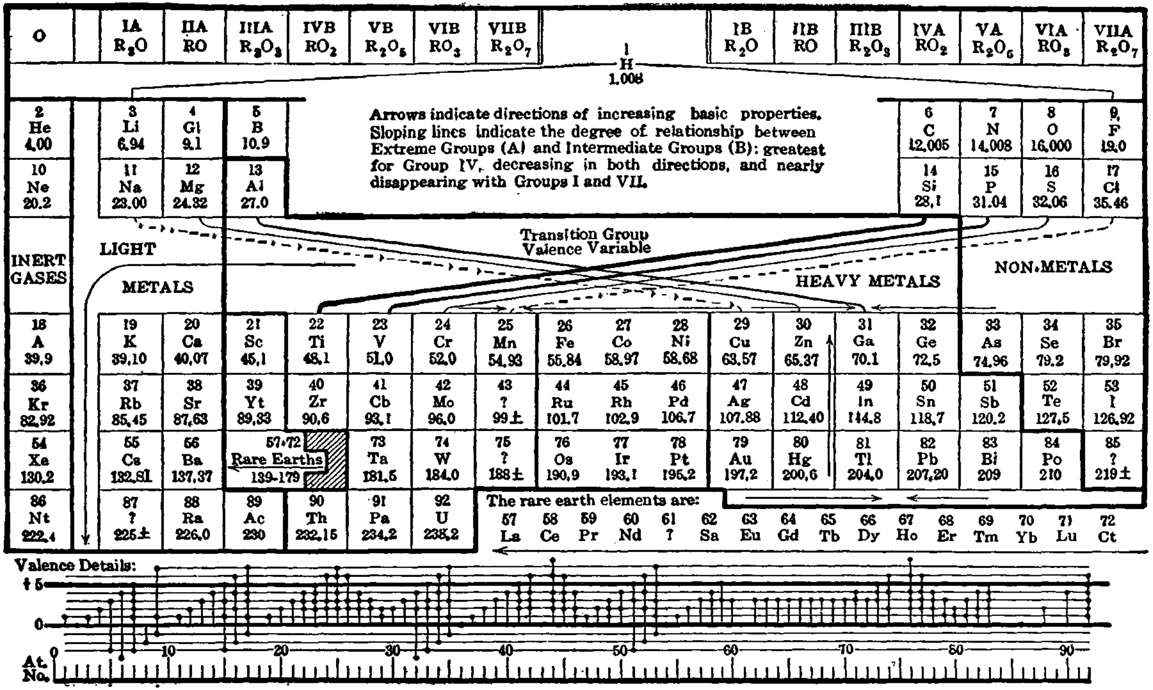
[1] Werner, *Ber.* **38** 914 (1905).

[2] Saul Dushman, *Gen. Elect. Rev.* **18** 614 (1915), and **20** 188 (1917). See inside front cover.

[3] Soddy, *Chemistry of Radioactive Elements.*

[4] Harkins and Hall, *Jour. Am. Chem. Soc.* **38** 169 (1916).

TABLE V



O	IA R_2O	IIA RO	IIIA R_2O_3	IVB RO_2	VB R_2O_5	VIB RO_3	VIIB R_2O_7				IB R_2O	IIB RO	IIIB R_2O_3	IVA RO_2	VA R_2O_5	VIA RO_3	VIIA R_2O_7
									1 H 1.008								
2 He 4.00	3 Li 6.94	4 Gl 9.1	5 B 10.9											6 C 12.005	7 N 14.008	8 O 16.000	9 F 19.0
10 Ne 20.2	11 Na 23.00	12 Mg 24.32	13 Al 27.0											14 Si 28.1	15 P 31.04	16 S 32.06	17 Cl 35.46
18 A 39.9	19 K 39.10	20 Ca 40.07	21 Sc 45.1	22 Ti 48.1	23 V 51.0	24 Cr 52.0	25 Mn 54.93	26 Fe 55.84	27 Co 58.97	28 Ni 58.68	29 Cu 63.57	30 Zn 65.37	31 Ga 70.1	32 Ge 72.5	33 As 74.96	34 Se 79.2	35 Br 79.92
36 Kr 82.92	37 Rb 85.45	38 Sr 87.63	39 Yt 89.33	40 Zr 90.6	41 Cb 93.1	42 Mo 96.0	43 ? 99±	44 Ru 101.7	45 Rh 102.9	46 Pd 106.7	47 Ag 107.88	48 Cd 112.40	49 In 114.8	50 Sn 118.7	51 Sb 120.2	52 Te 127.5	53 I 126.92
54 Xe 130.2	55 Cs 132.81	56 Ba 137.37	57-72 Rare Earths 139-179		73 Ta 181.5	74 W 184.0	75 ? 188±	76 Os 190.9	77 Ir 193.1	78 Pt 195.2	79 Au 197.2	80 Hg 200.6	81 Tl 204.0	82 Pb 207.20	83 Bi 209	84 Po 210	85 ? 219±
86 Nt 222.4	87 ? 225±	88 Ra 226.0	89 Ac 230	90 Th 232.15	91 Pa 234.2	92 U 238.2											

Arrows indicate directions of increasing basic properties. Sloping lines indicate the degree of relationship between Extreme Groups (A) and Intermediate Groups (B): greatest for Group IV, decreasing in both directions, and nearly disappearing with Groups I and VII.

The rare earth elements are:

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
La	Ce	Pr	Nd	?	Sa	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ct

Arrangement of H. G. Deming

one within the other, and the sequence of elements changes from the larger cylinder to the smaller as we pass from a long series to a short one. In this way the elements in the B division of a group fall behind the ones in the A division. The rare earth elements and the isotopes of the radioactive elements are arranged vertically along the surface of the helix parallel with its axis. A flat surface representation of this arrangement is shown in Fig. 2, but a model is needed to show the completeness of the system.

How Many Elements Are There? — In ancient times all forms of matter were supposed to be derived from the four "elements," — earth, air, fire, and water. Since this theory was overthrown there has never been a time when man could agree on the probable number of elements. At no time has the answer to this question been more nearly within reach than at the present. A study of the atomic numbers of the elements has led to the conclusion that from helium to uranium inclusive there are 91 elements, making with hydrogen a total of 92 possible elements within the limits of our present knowledge. Nearly all of the recent periodic arrangements also indicate the existence of 92 elements within these limits. It is a startling fact that in Mendeléeff's table, he placed the 63 elements known in 1871 and left enough blanks to make almost exactly a total of 92 elements. At first thought this appears to be a wonderfully accurate prediction, but upon close inspection it is found to be merely a strange coincidence. Only three of Mendeléeff's blanks have actually been filled. Some others may be filled by elements yet undiscovered, but most of his blank spaces never will be filled. He knew nothing of the Zero Group and the rare earth group was quite incomplete. So it is more probable that the number of elements for which his table provided was determined more by convenience than by any deep-seated conviction.

If the region between helium and uranium contains 91 elements then five are as yet undiscovered. These have been predicted and named: (1) eka-manganese with an atomic number 43 and an atomic weight approximately 100; (2) dwi-manganese, atomic number 75 falling between tungsten and osmium; (3) eka-iodine, atomic number 85; (4) eka-neodymium, a rare earth element of atomic number 61; and (5) eka-caesium of atomic number 87. Of these, greatest interest has

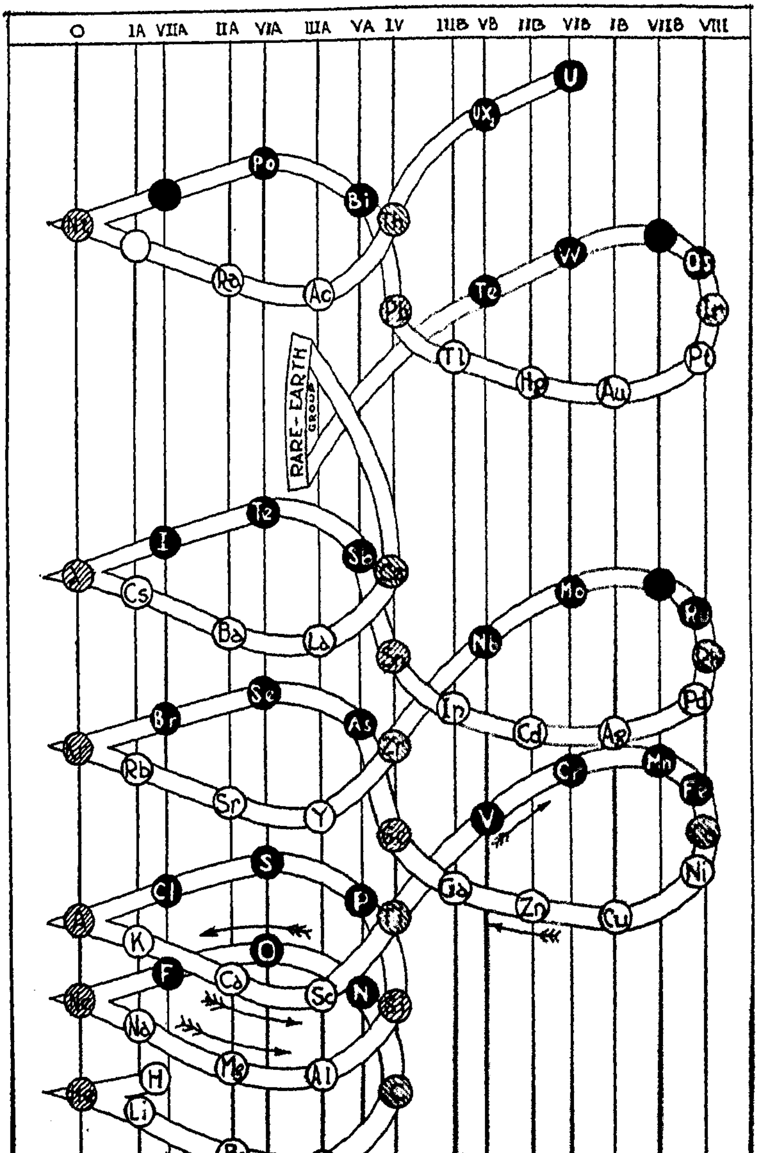


FIG. 1.—SODDY'S HELICAL ARRANGEMENT OF THE PERIODIC SYSTEM

Reproduced from the author's *Chemistry of the Radio Elements*, by special permission of Professor Soddy and his publishers, Longmans, Green and Co.

attached to the last named on account of the unsuccessful effort to locate the element. (See Caesium.) Some interest is also being shown in eka-manganese on account of the fact that its discovery was announced [1] by Ogawa, a Japanese chemist, who claimed that the element which he called nipponium, named from Nippon, a name for Japan, confirmed all the prophecies of Mendeléeff regarding this element. He has been accused of "faking" the whole report, since separate investigations by Sir William Ramsey and R. B. Moore have failed to verify his results.

In addition to the 92 elements already provided for, there are three regions of doubt: (1) before hydrogen, (2) following uranium and (3) between hydrogen and helium. Studies in radioactivity have suggested the possibility of atoms heavier than uranium, but the existence of such elements has never been demonstrated, and if they have ever existed on the earth they are doubtless unstable under conditions now extant. Hence, these are usually referred to as "extinct" elements (Bayley).

Spectrum analysis has given evidence of the existence of several unrecognized elements, some heavier than hydrogen and some lighter. The existence of a gas asterium,[2] unknown upon earth, is suspected in the hottest stars. Nicholson likewise suggests the existence of a series of simple elements, including arconium with an atomic weight 2.9 as calculated from the width of the spectral lines and by the differences between the calculated and observed wave lengths. Protofluorine with an atomic weight 2.1 is probably identical with coronium [3] first observed in the corona of the sun and later reported from the volcanic gases of Mt. Vesuvius. Nebulium [4] with a calculated atomic weight of 1.31 was reported present in the spectrum of certain nebulae, and is probably identical with aurorium reported in 1874 by Huggins [5] from a study of the spectrum of the aurora borealis. Protohydrogen has also been reported with an atomic weight of 0.082. Etherion was reported [6] by Brush at the Boston meeting of the American Association for the Advancement of Science in 1898. It was described as a gas which may be expelled from powdered glass and other substances under high temperatures and pressures less than $\frac{1}{1000000}$ of an

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[1] *Jour. Chem. Soc.* (Lond.) **94** 952.

[2] See *Chem. News*, **79** 145 (1899).

[3] *Chem. News*, **78** 43 (1898).

[4] *Chem. News*, **59** 161.

[5] See *Proceedings Roy. Soc.* 1899.

[6] *Trans. Am. Assoc. Sci.* Boston meeting; also, *Chem. News*, **78** 197.

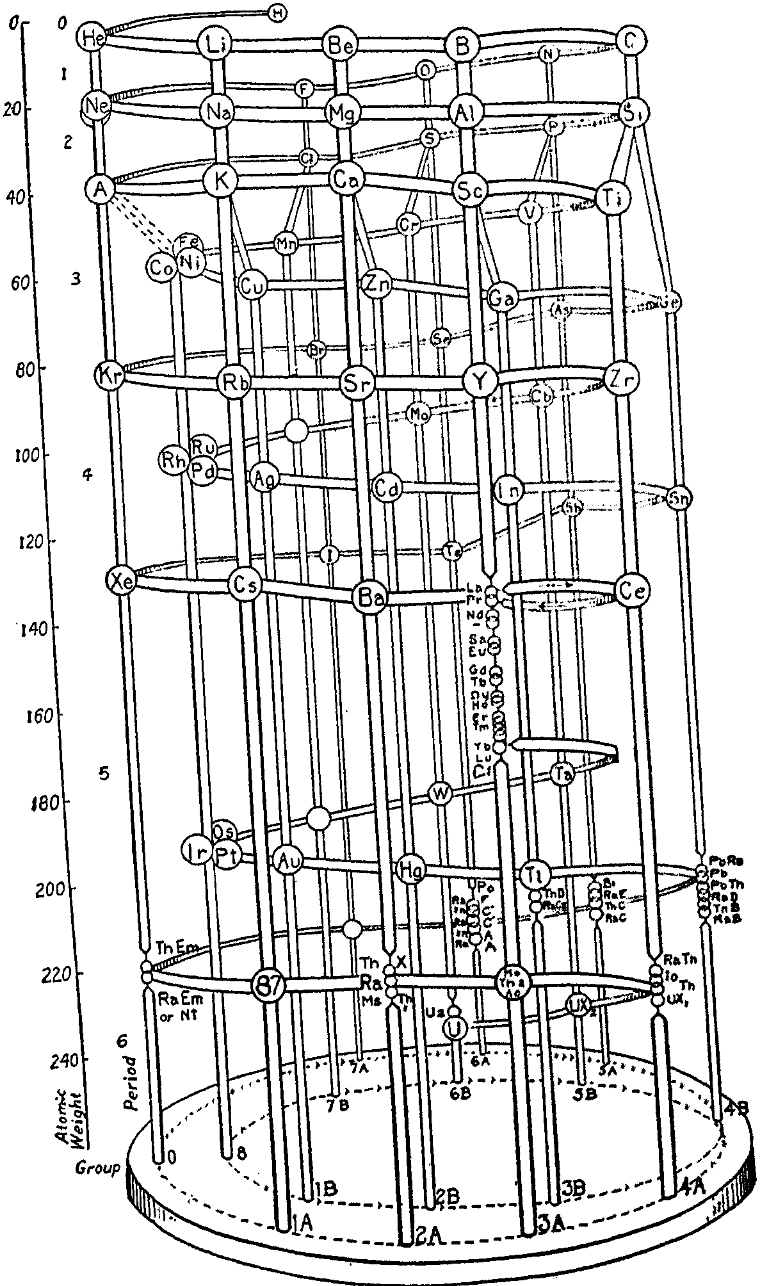

FIG. 2.—PERIODIC TABLE BY W. D. HARKINS

atmosphere. Its atomic weight was calculated as about $\frac{1}{1000}$ that of hydrogen, and it was described as possessing enormous heat-conducting power, but lacking in chemical affinity. From the manner of obtaining this gas and its general behavior Crookes suggests that the peculiar properties noted are due to the presence of water vapor, which would quite certainly be present under the conditions described and behave as the new " gas " did.

Efforts to prove the existence of such elements as these have made little progress because of the well-known variations in spectral lines produced by different conditions. Keeler[1] points out that entirely different spectra may be produced from an element by varying conditions. Thus, if the spectrum of an element is produced from various mixtures, new lines may be produced and others may disappear because of overlapping. Pressure influences the spectrum, usually producing a broadening of the lines.[2] Temperature produces so marked an effect[3] that it has been said that " a rise of 5° in temperature is sufficient to transfer D_1 to the position of D_2." Variations in the magnetic conditions produce enormous changes in the spectrum of an element.[4] On account of these facts chemists have been conservative in accepting the discovery of an element when our knowledge of its existence is based on spectroscopic evidence alone.

Discoveries of a very large number of new elements have been claimed in recent times. Charles Baskerville, in the presidential address delivered before the chemists of the American Association for the Advancement of Science, St. Louis, 1903, gives a list[5] of more than 180 such announcements since 1777. Of these only about 36 may be considered as actual discoveries of new elements, while over 130 have failed of confirmation or have been definitely rejected because the observations were made upon impure materials or upon elements already known. Of the remainder some may still be considered as having an undetermined status and others are what we now call isotopes.

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[1] *Sci. Am. Suppl.* **88** 977 (1894).

[2] Schuster, *Brit. Assoc. Report,* 275 (1880).

[3] See *Lieb. Ann.* **238** 57; *Chem. News,* **56** 51.

[4] Foote and Mohler, *Origin of Spectra*, American Chemical Society Monograph, chapter v, especially figures 23, 24.

[5] "The Elements, Verified and Unverified," *Chem. News*, **89** 109 *et seq.* (1904). See also Harkins, *Jour. Am. Chem. Soc.* **42** 1985 (1920).

CHAPTER II

THE ZERO GROUP

In many respects Group Zero is unique among the families of the periodic table. It is the only group whose elements are all gaseous at ordinary temperatures; all of these elements appear to be totally inactive chemically; this group and the Eighth are the only ones in which there are not represented rather definite odd and even sub-groups. This group is transitional between the extremely electro-negative halogens and the strongly electro-positive alkali metals. These elements are known as the " inert gases " on account of their chemical indifference; " noble gases " on account of their analogy to platinum and gold; or " rare gases " because, with the exception of argon, they are found in the atmosphere in extremely minute amounts. None of these gases so far as we know have color, odor, or taste, and their other physical properties furnish striking resemblances with a gradation similar to that found in other families. (See Table VII.) It is to be noted that the ratio between the specific heats at constant pressure and constant volume is quite uniform and the value 1.6 is generally interpreted as indicating that these gases are monatomic. The reasoning is, however, not conclusive and Mellor objects to the unqualified acceptance of this view.[1]

HELIUM[2]

Historical. — On August 18, 1868, a solar eclipse occurred, during which the sun's photosphere was for the first time studied with the aid of a spectroscope. P. J. C. Janssen[3] called attention to the fact that a certain line in the yellow supposed to be caused by sodium did not coincide with either D_1 or D_2 and proposed to call it D_3. Frankland and Lockyer[4] concluded that this line was due to an element unknown upon the earth, and suggested the name helium, the sun element. Later the same yellow line was detected in the spectrum of certain stars and it was reported in

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[1] Mellor, *Modern Inorganic Chemistry*, pp. 564 and 836.

[2] See "Helium, Its History, Properties, and Commercial Development," by R. B. Moore, *Jour. Frank. Inst.* **191** 145 (1921); for a bibliography of Helium, see Circular 81, Bureau of Standards (1919).

[3] *Compt. rend.* **67** 838 (1868).

[4] *Proc. Roy. Soc.* **17** 91 (1868).

TABLE VII

Physical Properties of the Noble Gases

	HE	NE	A	KR	XE	NT
Parts per thousand in Atmosphere — by volume	0.0014	0.015	9.37	0.00005	0.000006	—
Ratio of Specific Heats $\frac{Cp}{Cv}$	1.652	1.642	1.65	1.689	1.666	—
Wt. of a liter N. T. P. in grams	0.1786	0.9002	1.7818	3.708	5.851	9.97
Mol. wt. (at. wt.; $D = O_2 = 32$)	4.00	20.20	39.90	82.92	130.2	222.4
Critical Temp., Abs.	5°.19	44°.74	150°.6	210°.5	289°.6	377°.5
Critical Press. in Atmos.	2.26	26.86	47.996	54.3	58.2	62.5
Boiling Point, Abs.	4°.5	25°	86°	122°	163°.9	211°
Melting Point, Abs.	—	20° (?)	83°.4	104°	133°	202
Density of a Liquid at B. P.	0.154	—	1.3787[2]	2.155	3.06	About 5
Solubility in water[1]						
Absorption Coef. at 0°	0.0097	0.0114	0.0578	0.1105	0.242	0.510
Absorption Coef. at 50°	0.0108	0.0322	0.0257	0.0383	0.073	0.100
Thermal Conductivity $K \times 10^6$	33.86	—	38.94	—	—	—

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[1] *Zeit. elektrochem.* **25** 269 (1919); Cady, Elsey, and Berger found the value 0.00937 for 0° and 0.00817 for 30°; see *Jour. Am. Chem. Soc.* **44** 1456 (1922).

[2] Leduc. *Compt. rend.* **167**, 70 (1918).

1881 by Palmieri[1] in the spectrum of the gases from Mt. Vesuvius, although some question has been raised about the possibility of the latter observation.[2]

In 1889, Hillebrand published Bulletin, U. S. Geological Survey, No. 78, in which he described some experiments upon a gas which had been expelled from the mineral cleveite. This gas he supposed to be nitrogen, since it yielded nitrogen compounds. He noticed, however, that its behavior differed somewhat from nitrogen, but he failed to detect the presence of the new element helium.

In 1894, Sir William Ramsay was studying the gas obtained by heating powdered cleveite and found about 12 per cent of nitrogen, some hydrogen, and some argon; there was also a brilliant yellow line of the same wave length as D_3 of the solar spectrum. Kayser announced[3] the detection of helium in the atmosphere in 1895. The confirmation of the discovery of terrestrial helium was quickly made, but at first there was some doubt concerning its homogeneity and position in the periodic table. The color of the glow from a Plücker tube containing pure helium is yellow under a pressure of 7 millimeters and green at a pressure of 1–2 millimeters. This led to the belief[4] that helium was a mixture of two elements, but efforts to separate them went to prove[5] that the gas is homogeneous. So helium took its place in the periodic table as an element without chemical affinity.

In 1903, Ramsay and Soddy[6] announced the discovery of the fact that helium was a product of the atomic disintegration of radium, one gram of which produces about 0.45 cubic millimeter of helium per day. Later it was found that other radioactive substances also yield helium and that the charged helium atom is the alpha particle.

Occurrence.[7] — Helium is widely distributed in nature, though usually in small amounts. It makes up a considerable portion of the sun's atmosphere and is probably the principal constituent of the hottest stars. It is present in the earth's atmosphere in a proportion estimated as about 1 part in 185,000 by volume.[8] It has been detected in the gases evolved from certain mineral springs. King's Well at Bath, England, is estimated to yield 1000 liters of helium annually. It has been detected in at least one meteorite, which fell in Augusta County, Virginia. It has also been obtained from a large number

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[1] *Rendiconti R. Accad. di Napoli*, **20** 233 (1881).

[2] Nasini and Anderlini, *Atti R. Accad. Lincei*, **13** (v) i. 368 (1904).

[3] Kayser, *Chem. News*, **72** 89 (1895).

[4] Runge and Paschen, *Phil. Mag.* **40** (v) 297 (1895); Brauner, *Chem. News*, **74** 223 (1896); also *Nature*, **52** 520 (1895).

[5] *Proc. Roy. Soc.* **60** 206, 449 (1897); **62** 316 (1898); also *Nature*, **56** 380 (1897).

[6] *Proc. Roy. Soc.* **72** 204; **73** 346 (1903).

[7] See "Helium Bearing Natural Gas," by G. S. Rogers, U. S. Geol. Survey, *Professional Paper*, No. 121 (1921).

[8] Watson, *Trans. Chem. Soc.* **97** 810 (1910).

minerals, principally those containing radioactive and rare earth elements such as pitchblende, thorianite, monazite, fergusonite, samarskite, and euxenite; also, in carnallite, rutile, beryl, columbite, and native bismuth.

The most important source of helium from a commercial point of view resulted from the investigation of Cady and McFarland,[1] who found that the natural gas of Kansas nearly always contained helium, in some samples the amount present being from 1.5 to 1.84 per cent. It is from such sources that commercial helium is being developed.

Speculations[2] concerning the quantity of helium in the upper layers of the earth's atmosphere have led to the conclusion that at 50 miles above the surface there is twice as much helium as oxygen; at 100 miles the atmosphere is mainly helium and hydrogen, and at 500 miles these two gases are the only ones to be found. On the basis of this theory, it is estimated that the total mass of helium surrounding the earth would equal 11,000,000,000 tons. On the other hand, mathematical calculations[3] have indicated that a gas as light as helium would not remain permanently a part of the earth's atmosphere, but would be slowly radiated into space. If this conclusion is correct then helium must be present in interstellar space, and the constant amount in our own atmosphere must be the result of a balance between the loss of helium into space and the emission from terrestrial sources.

Separation. — Up to quite recently the cheapest method of obtaining helium was by heating a mineral, especially cleveite or monazite, either alone or with dilute sulfuric acid, or with potassium acid sulfate. When heated alone the finely ground mineral is placed in an iron or porcelain tube which is connected with a system for absorbing moisture and carbon dioxide. The system is evacuated and the tube heated to 1000°–1200° C. When treated with dilute acid the mineral is placed in a strong flask connected tightly with a condenser and funnel tube. Through the latter, 1 : 8 sulfuric acid is added and the former is connected with a pump by which the evolved gas is removed. Usually a better yield of helium is obtained by heating the mineral with

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[1] Jour. Am. Chem. Soc. **29** 1523 (1907).

[2] J. H. Jeans, *Dynamic Theory of Gases*, chapter XV.

[3] Stoney, *Chem. News*, **71** 67 (1895); see also Chapman and Milne, *Jour. Meteorolog. Soc.* **46** 357 (1920).

sulfuric acid. Approximately a liter of gas may be obtained from 200 grams of cleveite at an estimated cost of about $5. After long and patient effort, Onnes obtained about 2 cubic meters of helium by heating monazite sand. The cost has been estimated at approximately $1600 per cubic foot.

When the method of liquefying air was developed sufficiently to permit the use of liquid air in considerable quantities, helium mixed with neon was obtained from the first fractions in the commercial distillation of liquid air. Obviously no very large amount of helium can be obtained in this manner unless the production of liquid air becomes a considerable industry. This is by no means an impossible source of helium, since it is now seriously proposed to use liquid air in the operation of the blast furnace.

During the recent war a sudden and insistent demand for helium arose because of the desire to equip observation balloons with a light non-inflammable gas. This suggestion was what would normally be called a purely " academic " dream, since the largest amount of helium ever collected was probably that obtained by Onnes. The cost would be prohibitive. But the U. S. Bureau of Mines recalled the presence of helium in the so-called " wind gas " of Kansas as reported by Cady and McFarland. The need was urgent, and without time for suitable preliminary experiments the government erected plants for the recovery of helium from the natural gas of Texas and vicinity. The effort was successful, and at the signing of the armistice 150,000 cubic feet of helium, enough for three or four observation balloons, were ready to be shipped abroad.

The work continued for a time, since the importance of helium in aëronautics is fully recognized. Dr. Manning, formerly director of the Bureau of Mines, estimates[1] that it is possible to obtain 6,000,000 cubic feet of helium per week from American natural gas, provided the process of separation is perfected to the degree that gas containing 0.35 per cent helium can be utilized. It is also pointed out that the supply of helium is evidently decreasing rapidly and in 20 years the present available supply of helium may be exhausted. It has been suggested[2] that the best helium-producing gas fields should be sealed to conserve the supply.

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[1] *Jour. Ind. and Eng. Chem.* **12** 821 (1920).

[2] Dr. Joseph S. Ames, chairman of the National Advisory Committee on Aëronautics.

Three methods[1] of removing helium from natural gas have been used, all dependent on freezing out all the other gases. A plant using the Linde process was built at a cost of $300,000 and began operations March 6, 1918. By September of the same year it was producing 5000 cubic feet of 70 per cent helium per day. For carrying out the Claude process a plant costing about $150,000 began operations some weeks later than the Linde plant and gradually improved both the yield and purity of helium. The largest plant was built at Petrolia, Texas, at a cost of $150,000, and with an original capacity of 30,000 cubic feet of helium per day. Here the Jeffries-Norton process[2] is used under the direction of the Bureau of Mines. In December, 1922, the Fort Worth plant was producing 15,000 cubic feet per day, with a prospect of doubling that output shortly. The question of storage for such a quantity of gas becomes a serious problem. The cost is said to be less than 10 cents per cubic foot, with the prospect of a decrease to 5 or even 2 cents per cubic foot. Recent tests at the cryogenic laboratory in Washington indicate that it is possible to produce reasonably pure helium from natural gas by a single operation, thus materially reducing the cost.

Canadian supplies[3] were tested by experimental plants at Hamilton, Ontario, and Calgary, Alberta. The Ontario natural gas contains 0.34 per cent helium, while the Alberta supply contains about 0.33 per cent. A plant with a capacity of 56,000 cubic feet of natural gas per hour has been designed. A modification of the Claude oxygen-producing column is used. The helium produced has a purity of 85-90 per cent or better. The cost in the Alberta field is estimated at £10 per 1000 cubic feet, exclusive of containers.

Purification. — Helium is separated from the other inert gases by taking advantage of the fact that its boiling point is the lowest of all the gases of this family. Nitrogen and hydrogen may be removed with hot lime and magnesium or calcium; argon (and nitrogen) may be liquefied by liquid air; and neon and all other gases may be condensed with liquid hydrogen.

Purification may be made in other ways. (1) If helium which contains not more than 20 per cent of air, oxygen, or nitrogen is passed over cocoanut charcoal at the temperature of liquid air, practically all the other gases are absorbed and helium remains.[4] (2) Helium may also be purified[5] by taking advantage of the fact that it is absorbed by finely divided platinum, while nitrogen and neon are not. (3) Fused quartz at a tem-

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[1] See address of Dr. F. G. Cottrell as Perkin medalist, *Jour. Ind. and Eng. Chem.* **11** 148 (1919); also R. B. Moore, *Jour. Frank. Inst.* **191** 145 (1921).

[2] For the principles involved in the three processes for liquefaction of gases see Washburn, *Principles of Physical Chemistry*, 2d edition, pp. 309–313.

[3] *Jour. Chem. Soc.* **39** 252 R (1920). *Inst.* **191** 145 (1921).

[4] Dewar, *Proc. Roy. Soc.* **74** 122, 127 (1904); Claude, *Compt. rend.* **158** 861 (1914); *Jour. Chem. Soc.* **39** 252 R (1920).

[5] *Compt. rend.* **121** 394; *Proc. Roy. Soc.* **60** 449 (1897).

perature of 1100° is permeable to helium and hydrogen but not to other gases. This method is slow but gives a very pure product.

Properties. — The constants for the principal physical properties of helium are given in the table on page 21. The properties which make helium most interesting are its lightness, its close approach to a perfect gas, its close relationship to the radioactivity and the composition of atoms, and its absolute chemical inactivity.

The density of gaseous helium has been determined by many investigators, the two best results being those of Watson[1] and Heuse.[2] The weight of a liter under normal conditions is given as 0.1782 g. and 0.17856 g. respectively. Thus, helium should have about 93 per cent as much lifting power as hydrogen. Experiment has shown[3] that 1000 cubic feet of helium will lift 69.58 pounds, while the same amount of hydrogen will lift 75.14 pounds.

As would be expected with so light a gas, helium diffuses rapidly, but not so rapitlly as would be expected from Graham's Law of Diffusion. Hydrogen and helium are the only gases which diffuse more slowly than would be expected from the kinetic theory. The penetrability of these two gases through balloon fabrics has been determined[4] as between 5 and 10 liters of gas per hour per square meter of fabric. Helium diffuses 0.71 as fast as hydrogen.[5] Hydrogen and helium diffuse readily through heated quartz at high temperatures and through silica glass at temperatures above 300°. Jena glass is not permeable to hydrogen but is to helium.[6]

The coefficient of compressibility is zero[7] between pressures of 147 mm. and 838 mm. of mercury at 0°; that is, the product of pressure times volume is a constant within this range. Onnes[8] has determined the isothermals for *pv* over a wide range of temperature and pressure.

The boiling point of helium is the lowest of all known sub-

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[1] *Trans. Chem. Soc.* **97** 810 (1910).

[2] *Ber. deutsch. physikal. Ges.* **15** 518 (1913).

[3] *Min. and Sci. Press.* **119** 306 (1919).

[4] *Phil. Mag.* **40** 672.

[5] *Jour. Ind. and Eng. Chem.* **12** 821 (1920).

[6] Williams and Ferguson, *Jour. Am. Chem. Soc.* **44** 2160 (1922).

[7] Burt, *Trans. Faraday Soc.* **6** 19 (1910).

[8] *Proc. K. Akad. Wetensch.* Amsterdam **10** 445, 741 (1907).

stances. It was the last of the so-called permanent gases to yield to the efforts to produce a liquid. The classical work of Kammerlingh Onnes[1] used 300 liters of helium gas, which was cooled first by liquid air, then by liquid hydrogen boiling under diminished pressure, and finally by passing through a special Hampson liquefier. Helium must be cooled to 15° A. before the Joule-Thomson effect will produce liquefaction. But at the temperature of solid hydrogen the expansion of helium from high pressure produces a sufficient lowering of the temperature to cause liquefaction. In this way Onnes produced 60 cc. of liquid helium.

Liquid helium is, next to hydrogen, the lightest liquid known. Its density[2] at 4°.33 A. is 0.1208 and at 2°.4 A. it is 0.1459. The temperature of maximum density is 2°.2 A., the critical temperature is 5°.25 A., and the critical pressure 2.26 atmospheres. Liquid helium is colorless, very mobile with very small surface tension. When evaporated under diminished pressure a temperature as low as 2°.5 A. was obtained,[3] but no solid helium resulted. Onnes failed to obtain solid helium at a temperature of 0.82° A.

Positive ray analysis[4] indicates that helium is a simple element without isotopic modifications. On the other hand a study of the atomic structure has led to the conclusion[5] that helium contains two types of atoms, which are designated as helium and parhelium. A study[6] of the probable constitution of the atoms of oxygen, nitrogen, and carbon suggests the value 3.0011 as the atomic weight of the isotope called isohelium (Rutherford's X_3). Helium atoms when subjected to certain voltages are ionized and remain in this metastable condition for about 0.0024 second.[7]

The dielectric cohesion[8] of helium at 17° is represented by 18.3 as compared with argon = 38, air = 419, hydrogen = 205.

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[1] *Proc. K. Akad. Wetensch.* Amsterdam, **11** 168 (1908); also *Compt. rend.* **147** 421 (1908).

[2] Onnes, *Comm. Phys. Lab.* Leyden, No. 119.

[3] Onnes, *Proc. K. Akad. Wetensch.* Amsterdam, **12** 175 (1909).

[4] F. W. Aston, *Phil. Mag.* **39** 611 (1920).

[5] J. Franck and F. Reiche, *Z. Physik*, **1** 154 (1920).

[6] M. C. Neuburger, *Physik Z.* **23** 145 (1922).

[7] Kannenstine, *Astrophysical J.* **55** 345 (1922).

[8] The dielectric cohesion may be explained as a constant which expresses the relative electrostatic field of force which is needed to render the gas a conductor of electricity.

An unusually long spark gap is therefore possible in helium, in which a spark of 250–300 mm. has been obtained [1] under the same conditions as produced a spark of 23 mm. in oxygen, 33 mm. in air, 39 mm. in hydrogen, and 45.5 mm. in argon.

Helium seems to have the ability to form solid solutions with finely divided platinum, with magnesium, and probably also with a considerable number of minerals, but there is no evidence of any chemical reaction involving helium. In a most thorough investigation,[2] Ramsay circulated helium at red heat over a long list of materials and was able to detect no change in either constituent. Efforts to make helium enter into combination under the influence of the silent electric discharge have been unsuccessful. It is therefore evident that helium is unable to enter into chemical reactions of the usual type.

Uses. — The most spectacular use of helium is for filling balloons in time of war. The cost is still considerable, but the advantages are numerous. Its total non-combustibility makes it possible to build a dirigible balloon more compactly because fear of sparks from the motor is removed. It has been suggested that it would be possible to mount a machine gun on the top of the gas bag. In order to decrease the cost, it has been proposed to put helium into the compartments which are exposed and hydrogen into other compartments. Another plan is to mix hydrogen with helium, since it has been demonstrated that as much as 20 per cent hydrogen is needed to produce an explosive mixture.[3] In a test flight early in December, 1921, the U. S. naval airship C-7 demonstrated the practicability of helium-filled dirigibles. In the flight from Hampton Roads to Washington and return it was unnecessary to lose any helium by valving, and the men in charge report that greater speed was developed and the ship maneuvered better than when filled with hydrogen. The fact that helium is a poorer conductor of heat than hydrogen eliminated much of the difficulty arising from variations in the lifting power of different portions of the gas bag, so the airship responded more definitely to its controls.[4]

There are certain problems to be overcome before helium can be called an ideal gas for use in balloons. Its scarcity

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[1] Collie and Ramsay, *Proc. Roy. Soc.* **59** 257 (1895).

[2] Ramsay and Collie, *Proc. Roy. Soc.* **60** 53 (1896).

[3] *Jour. Chem. Soc.* **39** 252 R (1920).

[4] See note, *Chem. and Met. Eng.* **25** 1111 (1921).

makes the cost extremely high and prevents the valving of the gas when it is desired to descend or to deflate the gas bag. The relatively inexpensive hydrogen is allowed to escape into the air, but helium must be compressed into cylinders, repurified, and used over again. Since the lifting power of helium is less than hydrogen, a balloon which is to use the former gas must have a gas bag approximately one-tenth larger than would be required in a hydrogen balloon. If an altitude of 10,000 feet is to be reached, as is necessary in crossing the Rocky Mountains, a helium gas bag can only be filled to 70 per cent of its capacity to provide for the expansion of the gas at these altitudes. Devices are being planned for compressing the gas, but these mean increased weight, decreased fuel capacity, and a corresponding limitation in cruising range.

The most important scientific use of helium is probably in connection with studies in radioactivity and extremely low temperature work. A study of helium will undoubtedly throw light on the nature of radiation, atomic structure, and other related problems. At the temperature of liquid helium, tin, lead, and mercury lose their electrical resistance; for example, a thread of mercury, which has a resistance of several hundred ohms at room temperature, when cooled to 2°.45 A. has less than two ten-billionths of its zero resistance. Other interesting and valuable results may be expected from the use of liquid helium in the cryogenic laboratory at Washington.

As an inert gas helium is useful for filling tungsten lamps which are to be used for signaling, because of the rapid dimming which results. Helium arc lights give an intense red and yellow light which has certain advantages over the mercury vapor lamp. In Geissler tubes helium furnishes a good standard light in spectrophotometry.

A number of other applications have been suggested, such as its use in mixture with oxygen for deep-sea divers, the purpose of which is to prolong the period of submergence by causing the more rapid exhalation of carbon dioxide; to replace oil for surrounding switches and circuit breakers for high-tension electric transmission lines; for filling thermionic amplifying valves of the ionization type.

Detection. — Helium is detected by its spectrum, the most prominent lines being the D_3 line which led to the discovery of the element and a prominent green line λ 5016. There are many other lines in the spectrum, whose intensity varies with the pressure.

If the sample under examination contains other gases than helium, these may be effectively removed by coconut charcoal cooled with liquid air.

Estimation. — The purity of a stream of helium may be continuously recorded by an automatic device developed at the U. S. Bureau of Standards. Its operation depends upon the thermal conductivity of the gas. When only two gases are present the apparatus gives accurate results; consequently it is serviceable in dealing with helium of a purity above 70 per cent, since nitrogen is the only impurity in such material.

A rapid method of determining the amount of helium in a mixture is based upon the rapidity with which the gas flows through a minute hole in a piece of platinum foil. The instrument is calibrated against pure nitrogen and a determination requires 2–3 minutes. An accuracy of 1–2 per cent is possible in a gas containing 20 per cent or more of helium and only one other gas.

NEON

Historical. — As soon as it became evident that helium and argon were members of a zero group of elements, search was made[1] for an element whose atomic weight would place it between helium and argon and just before sodium. For this purpose 18 liters of argon gas were prepared from liquid air and condensed to a liquid. By several distillations of this liquid the element neon (from the Greek word meaning "new") was isolated from the more volatile portion. The gas was not again obtained in pure form until 1910; consequently, its development has been very slow.

Occurrence. — Neon occurs in the atmosphere in proportion of one volume to about 55,000 volumes of air. It has also been detected in some samples of natural gas and in the gases evolved by certain hot springs.

Separation. — Neon is the most difficult of the rare gases to obtain in pure form, not only because it is present in the air in very small amounts, but also because it collects in the middle fractions which are the most difficult to purify.

Several modifications of Ramsay's method of fractionation have been devised and used to separate neon. The most successful method for working with a large amount of material uses a modification of Claude's apparatus, in which fractionation is accomplished by a fractionating column. By this means all the hydrogen, helium, and neon of the air are separated, with some nitrogen, as the light gas. From this, nitrogen is removed by hot magnesium or cold charcoal.

A simple method of separating neon from the other gases is

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[1] Ramsay and Travers, *Proc. Roy. Soc.* **63** 316 (1898); **63** 437 (1898).

to use the selective absorption of charcoal cooled in liquid air, devised by Dewar. Charcoal cooled to − 100° C. absorbs argon, krypton, and xenon completely, but scarcely absorbs helium and neon at all. At a temperature of − 180° to − 190° C., neon is absorbed and helium left in gaseous state. From the charcoal the occluded gases are easily obtained by raising the temperature. If nitrogen is present it also may be removed by cooled charcoal, since it is more readily absorbed than either neon or helium.

Properties. — Neon resembles helium closely, but shows a greater variation from the expected values than any other member of the family. (See Table VII, page 21.)

Watson[1] has determined that a liter of neon weighs 0.90002 grams under normal conditions. This corresponds closely to the accepted molecular weight, 20.2.

The dielectric cohesion of pure neon at 17° is 5.6, much below that of helium and the lowest for any gas. This value is materially raised by the presence of impurities; consequently, the purity of any sample of neon may be judged by the determination of this constant.

Neon diffuses through quartz at 1000° C., but less readily than helium.

When neon is shaken with mercury or heated unequally a marked red glow appears. The explanation offered for this curious behavior is that there is developed a difference of potential which is sufficient to produce a glow in the neon on account of its high conductivity.

Neon may be liquefied at atmospheric pressure by surrounding it with boiling liquid hydrogen; it may also be solidified by allowing the hydrogen to boil under diminished pressure.

Using his positive ray analysis, J. J. Thomson has shown that atmospheric neon contains two isotopes, one with an atomic weight 20 and the other 22. This conclusion has been confirmed by Aston,[2] who obtained evidence of two isotopes of atomic weights 20 and 22 in proportion 9 to 1. This accounts for the accepted value of 20.2. There is also some evidence of a third isotope of value 21, comprising about 1 per cent of the whole. If this conclusion is confirmed this would furnish an interesting triad somewhat similar to those found in Group VIII.

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[1] *Trans. Chem. Soc.* **97** 826 (1910).

[2] *Nature*, **92** 308 (1913); *Phil. Mag.* **39** 449 (1920).

Uses.—Several types of neon lamps have been designed,[1] the advantage being that the penetrating red rays are valuable for signaling. The light is produced by the glow discharge at the cathode and the intensity is dependent upon the area of the cathode surface and the pressure of the gas. With a voltage of 220 the glow begins instantly, and when used for stroboscopic work the working flash has a maximum duration of one two-millionth of a second. Such a lamp has great value in measuring the velocity of revolution and in many other engineering problems. The economy of the neon lamp is shown by the statement that a Moore tube filled with neon containing a little helium consumed 0.26 watts per Hefner candle, while a similar tube filled with argon consumed 45 watts. Lamps containing as much as 25 per cent helium are as efficient as those containing pure neon. Various electrodes are used, iron and aluminium being the most common; an alloy made up of 82 per cent thallium and 18 per cent cadmium is especially successful as the cathode. The lamps burn for 2000–3000 hours. It has been found[2] that a neon lamp produces one hundred times as much luminosity for the same current consumption as can be obtained with argon.

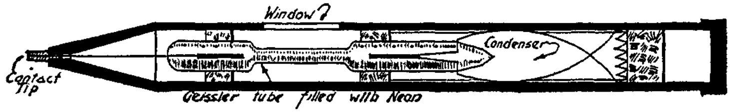

FIG. 3.—SPARK PLUG TESTER

A neon lamp[3] has recently appeared on the market which is recommended for use in halls, hospitals, and other places where subdued light is desired. It is rated at about 5 watts and is supplied for both direct and alternating currents. The economy in its use comes both from its long life and the saving of electrical energy when compared with the present methods of producing reduced electrical illumination.

The ease with which an electric spark will pass through neon has been utilized in devising a spark plug tester for use

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[1] *Elektrochem.* **24** 131, 132 (1918); *Elektrochem. Z.* **40** 186 (1919); F. W. Aston, *Proc. Cambridge Phil. Soc.* **19** 300 (1919).

[2] D. McF. Moore, *Jour. Am. Inst. Elect. Eng.* **39** 732 (1920).

[3] Phillips lamp; see *Electrician*, **87** 25 (1921); another type is the Pintsch lamp, described in *Elektrochem. Z.* **42** 121 (1921).

with internal combustion engines. These little instruments[1] are serviceable not only for locating ignition troubles in an automobile, but also are suggested for use in a factory where the development of frictional electricity by the moving machinery might cause a dust explosion.

The neon spectrum lines are sharp and furnish a good standard light source, especially between 3369 A. and 3520 A.

Detection. — Neon is identified by its brilliant spectrum lines, especially prominent in the orange and red regions.

ARGON

Historical. — In 1785, Cavendish published[2] an article describing an experiment in which he passed an electric spark through a volume of air mixed with an excess of oxygen and absorbed the products in an alkaline medium. After removing all the nitrogen the residual oxygen was absorbed, when there remained a gas which was neither oxygen nor nitrogen. Cavendish estimated the amount of this gas to be not more than $\frac{1}{120}$ of the total nitrogen. This experiment was forgotten for over a century.

In the years 1893–95, Lord Rayleigh was studying the weights of various gases from different sources. A liter of nitrogen from the air weighed 1.2572 g. while nitrogen prepared chemically weighed 1.2505 g. per liter. The difference was much larger than the experimental error, and an examination of the "chemical" nitrogen failed to show the presence of any light impurity. So the conclusion was necessary that the "atmospheric" nitrogen must contain some constituent heavier than nitrogen itself. With the coöperation of Sir William Ramsay, and the suggestion furnished by Cavendish's experience, it was discovered that when all the known constituents of the air were removed there always remained a residue which was proportional to the volume of air used. This residue was shown[3] to differ from nitrogen both spectroscopically and chemically as well as in density. The new gas was named argon, meaning "inert," because of its chemical inactivity. This discovery has been spoken of as the "Triumph of the Fourth Decimal," because of the experiences leading to the announcement.

The year 1894 saw the discovery of both argon and helium, but the former was definitely isolated some months before the latter. Immediately there arose a question as to the position of argon in the periodic table. This problem became all the more puzzling because of the fact that argon has a higher atomic weight than potassium which it precedes. The opinion that argon should be placed in Group Zero before potassium received confirmation from the discovery of helium, but the status of both elements was not fully established until after the discovery of the other elements of this group.

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[1] *Chem. and Met. Eng.* **26** 703 (1922); *Jour. Ind. and Eng. Chem.* **14** 160 (1922).

[2] *Phil. Trans.* **75** 372 (1785).

[3] Rayleigh and Ramsay, *Phil. Trans.* **186** 187 (1895).

Occurrence. — Argon is a very constant constituent of the air, of which it comprises 0.94 per cent by volume, which is equivalent to 1.18 per cent by volume of atmospheric nitrogen. The per cent of argon varies only slightly in samples taken from various localities on land, but over the sea the per cent of argon is slightly more,[1] up to 0.949 per cent. Altitudes as great as 3½ miles have failed to show [2] any material change in the quantity of argon present. The fact that argon is more soluble in water than is nitrogen accounts for the fact that the proportion of argon in dissolved gas is greater than in air; it also probably accounts for the fact that argon is found in plants and in the blood of animals.

Argon is likewise a constituent of volcanic gases and gases from mineral springs, where it sometimes runs as high as 4.5 per cent. It is found in certain samples of natural gas, and a few minerals, mainly zirconium ores, yield argon when heated. The atmosphere is supposed to be the original source of argon in nearly all cases.

Separation. — Argon is always prepared from the atmosphere, the methods used being more or less simple modifications of the methods used by Rayleigh and Ramsay.[3] From atmospheric "nitrogen" the nitrogen may be removed by hot magnesium, lithium, calcium, a mixture of 5 parts lime and 3 parts magnesium powder (Maquenne's mixture), or a mixture of 90 parts calcium carbide and 10 parts calcium chloride. Argon for electric lamps is purified [4] by passing the gas under increased pressure through electrically heated furnaces containing copper and copper oxide. Commercial oxygen generally contains [5] about 3 per cent argon, and this may be recovered by distillation and removing the last of the oxygen with hot iron or copper, and the nitrogen by calcium turnings.

Prepared in this way the argon always contains about 0.25 per cent of the other inert gases, chiefly neon. These are best removed either by fractional distillation of the liquid or by the fractional absorption in cold charcoal.

Properties. — The constants for the chief physical properties of argon are given in Table VII, page 21.

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[1] Moissan, *Compt. rend.* **137** 600 (1903).

[2] Schloesing, *Compt. rend.* **123** 696 (1896).

[3] *Trans. Chem. Soc.* **71** 184 (1897).

[4] *Chem. and Met. Eng.* **25** 74 (1921).

[5] Bodenstein and Wachenheim, *Ber.* **51** 265 (1918).

A liter of argon weighs 1.782 grams, corresponding to the molecular weight of 39.9.

Argon is about 2½ times as soluble in water as is nitrogen. At ordinary temperatures 100 volumes of water will dissolve about 4 volumes of argon.

Argon diffuses through a fine opening about 3½ times as fast as would be expected by comparison with oxygen.

Argon has the highest viscosity of all the principal gases — about 1.2 times that of air.

The dielectric cohesion of argon is 38, ranking next to helium and neon. The sparking distance in argon is about 40 per cent greater than in air. A phosphorescence similar to that obtained in neon has been observed.

When a continuous current at 2000 volts is passed through argon under diminished pressure, a red glow results; but an oscillating current produces a blue color. Two spectra are therefore recognized, the red and the blue. Both contain a large number of lines.

Argon is easily liquefied by the use of liquid air. Liquid argon is colorless, with a density 1.4. Solid argon, obtained by cooling the liquid, is a white crystalline substance whose melting point is less than 3° below the boiling point.

The chemical inertness of argon has been demonstrated by even more tests than were used in the case of helium. The results are all clearly negative with the possible exception of the effect of the silent electric discharge upon a mixture of argon with volatile aromatic compounds.[1] Argon was absorbed under these conditions, but there is no evidence of the formation of any compounds.

Under pressures of 150 atmospheres pure argon is said to condense with ice water, forming a solid crystalline hydrate.

Argon has been shown [2] to have two isotopic forms, one with an atomic weight of 40 making up 97 per cent, and the other with an atomic weight of 36.

Uses. — Argon is the most efficient of the available gases for filling incandescent light bulbs, because of its low thermal conductivity, its inertness, and its density which holds in check

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[1] Berthelot, *Compt. rend.* **120** 581, 1316, 1386 (1895); **124** 113 (1897); **129** 71, 133, 378 (1899).

[2] Aston, *Phil. Mag.* **39** 620 (1920).

the vaporization of the tungsten filament and prolongs its life. Consequently, they are especially serviceable in lamps which are to be used with an electric current of high density. Gas-filled lamps are rapidly replacing the vacuum lamps on account of the appreciable economy in their use. Roughly, half the lamps sold in 1919 were gas filled, and of these argon lamps were most efficient for currents of high density. In December, 1922, it was estimated that 75,000 cubic feet of argon were consumed in the United States each month in the manufacture of incandescent lamps. The "tungar" rectifier, a charging device using a tungsten filament in an argon bulb, is also rapidly becoming popular.

Detection. — Argon is detected spectroscopically, but the complete removal of nitrogen is essential, since its presence obscures the characteristic argon lines. As much as 37 per cent argon in nitrogen can with difficulty be detected by the spectroscope. The purity of argon may be indicated by the determination of its dielectric cohesion, since 1 per cent of any diatomic gas increases this constant 250 per cent.

KRYPTON

Historical. — When Ramsay and Travers were working upon the separation of argon, they fractionated[1] 30 liters of liquid air, and from the less volatile portions they separated a gas which resembled helium, neon, and argon in general characteristics. This gas had a density 22.5 on the basis of H = 1, and gave an entirely new spectrum. This gas was named krypton, the hidden element. Ladenburg and Krügel[2] evaporated 850 liters of liquid air and obtained the same results.

Occurrence. — Krypton is found in the atmosphere in the proportion of about 1 part in 20,000,000. It is present in slightly larger amounts in the gases evolved from certain mineral springs.

Separation. — Krypton has never been obtained except from the atmosphere. A convenient method of separation consists in passing a slow stream of dry oxygen, which has been materially enriched by fractionation in a liquid air plant, through a tube cooled with liquid air. In this way krypton and xenon together with a little argon condense as a liquid or solid.

Pure krypton may be prepared by slowly warming the solid mixture and pumping away the gas first liberated; charcoal cooled to − 120° dissolves all the krypton and xenon with only

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[1] *Proc. Roy. Soc.* **63** 405 (1898).

[2] *Sitzungsber. K. Preuss. Akad.* (1900), page 727.

a little argon. The latter is removed by exposure to fresh charcoal cooled in liquid air, and krypton is then expelled by allowing its bulb to warm up to −80° C. Repeated fractionation is essential for obtaining pure krypton.

Properties. — For the principal physical constants see Table VII, page 21. The density of krypton was determined[1] from the purest material obtained by the fractionation of 120 tons of liquid air. From the data obtained a liter of krypton weighs 3.708 grams. The molecular weight is therefore calculated to have the value 82.92.

The spectrum of krypton shows marked peculiarities. When the direct discharge is used the lines are few in number and chiefly in the yellow, blue, and green. By the use of a Leyden jar and spark gap a large number of blue lines are visible. The most persistent line is λ 5570 which may be seen at pressures as low as $\frac{1}{23 \times 10^6}$ atmospheres. It was formerly supposed that the weird beauty of the aurora borealis was in part due to krypton, since the lines of this element were thought to have been identified in the spectrum of the aurora. Recent investigation seems to cast doubt upon this conclusion.

Since krypton has a boiling point of −151°.7 C. it is easily liquefied at the temperature of liquid air.

Krypton probably has six isotopes, whose atomic weights are given[2] as 78, 80, 82, 83, 84, and 86.

Identification. — Krypton is identified by its characteristic spectrum lines. The quantity of krypton in any gas may be determined[3] by spectrophotometry.

XENON

Historical. — The discovery of xenon was made at the same time and in the same investigation that revealed the presence of krypton. Xenon, which is heavier than any of the preceding noble gases, was obtained from the least volatile portions of liquid air. The name xenon signifies a stranger.

Occurrence. — Xenon is the rarest of the inert gases, being found in the atmosphere to the extent of approximately 1 volume in 170,000,000 volumes of air. Its solubility in water is greater than any of the other members of the group except niton, which

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[1] Moore, *Trans. Chem. Soc.* **93** 2181 (1908).

[2] Aston, *Phil. Mag.* **39** 623 (1920).

[3] Moureu and Lepape, *Compt. rend.* **174** 908 (1922).

explains its presence in the gases of many mineral springs.[1] It is isolated only from the atmosphere.

Separation.—In spite of its scarcity, xenon is quite easily prepared in a pure state because it is concentrated in the least volatile fractions. The separation may be accomplished by the fractional distillation of considerable quantities of liquid air as suggested under krypton. The most convenient way of getting xenon is by passing liquid air residues through a tube filled with glass wool and cooled by liquid air. By carefully regulating the temperature and pressure it is possible to obtain solid xenon with only small percentages of other gases occluded. The vapor pressure of solid xenon is only 0.17 mm. at the temperature of liquid air, so it is fairly easy to pump off all more volatile gases. The small fraction of krypton which is entrapped may be almost entirely removed by melting the solid, then repeating the process.

Properties.—(See Table VII, page 21.) The density of xenon was determined by Ramsay and Travers[2] working with only 3 cc. of the gas. But the value obtained by Moore, using the purest product from his 120 tons of liquid air, is far more accurate. His work gives the weight of a liter at standard conditions as 5.851 g. This corresponds to a molecular weight of 130.22.

Like helium and krypton, xenon has two spectra, depending on the method of production. An uncondensed discharge through xenon gives a light blue color, while a condensed discharge produces a green. The lines in the latter are especially numerous.

The critical temperature of xenon is 16°.6 above the melting point of ice. Consequently in a cool room the gas may be condensed without artificial cooling, a pressure of 58.2 atmospheres being necessary.

Liquid xenon is colorless with a density of 3.06 at its boiling point, −109°.1 C. The density varies widely with temperature, being 2.694 at −59°.3, 1.987 at 0°, and 1.468 at 16°.

Solid xenon is easily prepared by cooling the liquid.

Work with a small amount of impure xenon has led[3] to the conclusion that the element is known in five isotopic forms.

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[1] Moureu and Lepape, *Compt. rend.* **149** 1171 (1909).

[2] *Phil. Trans.* **197** 47 (1901).

[3] Aston, *Phil. Mag.* **39** 623 (1920).

Identification. — The detection of xenon is accomplished by its characteristic spectrum lines. The quantitative determination may be done by spectrophotometry.[1]

NITON[2]

Historical. — In studying the phenomena of radioactivity the Curies observed that nearly any substance when brought near to radium acquired an induced radioactivity. The intensity of this induced radioactivity was found to be proportional to the time of exposure, up to a certain limit, and decreased rapidly after the radium was removed. Rutherford studied this behavior and found that the phenomenon was due to the continuous evolution of a colorless substance which was itself highly radioactive. This substance behaved like a gas, but Rutherford proposed to call it an "emanation" since at first it was not certain that it was to be properly designated as a gas. Careful study has, however, revealed convincing evidence that it is a radioactive gas, resembling the inert gases and properly placed in the Zero Group. The name niton has now pretty generally replaced the former name radium emanation. Isotopic with niton are the gases actinium emanation and thorium emanation.

Occurrence. — Niton is probably present in all radioactive minerals, but always in infinitesimal amounts. Since it disintegrates rather rapidly, it is always a transition product, in equilibrium with the radium present. Since this element is itself present in very small amounts, the quantity of niton in any mineral must be exceedingly small.

The presence of a radioactive gas in the atmosphere has been demonstrated[3] by the simple exposure of a negatively charged wire. There was collected upon the wire a deposit itself radioactive, soluble in ammonia, or removable by rubbing. Study of this deposit has shown that it is a mixture of solids including radium A, radium B, radium C, etc., and thorium A, thorium B, thorium C, etc. These substances are obtained from the emanations of radium and thorium. The proportions of the two vary considerably in various localities, but in general the proportion of niton is greater at higher altitudes and the amount of thorium emanation increases at lower levels. The amount of niton present in a cubic meter of air is estimated to be that which would be in equilibrium with 1.0×10^{-10} grams of radium.

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[1] Moureu and Lepape, *Compt. rend.* **174** 908 (1922).

[2] The newly organized International Committee on Chemical Elements recommends the name radon, with symbol Rn, for the element formerly called niton. *Chem. News*, **126** 145 (1923) and *Jour. Am. Chem. Soc.* **46** 867 (1923).

[3] Rutherford and Allen, *Phil. Mag.* **4** (vi) 704 (1902); Allen, *ibid.* **7** (vi) 140 (1904).

Separation. — Niton is normally given off slowly but continuously from radium and its salts. If the radium material is heated to about 800° C. the gas is expelled almost wholly Since the maximum amount of niton which can be in equilibrium with a gram of radium is 0.585 cubic millimeters, the amount of niton obtainable at any time is exceedingly small. It is customary to wash the niton out of the tube with some other gas such as oxygen.

When an aqueous solution of radium salt is kept in a closed flask, there is a continuous evolution of niton, hydrogen, and oxygen. The last two are produced by the decomposition of water by the radium. The proportion of hydrogen is from 5–10 per cent more than would be expected from the amount of oxygen present. This is explained by the action of the penetrating radium rays in converting water into hydrogen peroxide and hydrogen. Niton obtained from solution is purified by first exploding the hydrogen and oxygen, then cooling the residual gas. In this way niton is condensed, forming microscopic globules of a liquid. It is possible then to pump off the remaining hydrogen together with the helium which forms from the disintegration of niton.

A small amount of niton has been prepared[1] from the atmosphere by a similar method.

Properties. — Niton is pretty certainly a gas, for it has a characteristic spectrum which is somewhat like that of xenon; it obeys Boyle's Law; it can be liquefied and solidified and has definite melting and boiling points. It is colorless by transmitted light. It is chemically inert and so is placed in the Zero Group.

The density of niton has been determined[2] by direct weighing on the microbalance, using about $\frac{1}{1400}$ milligram of the gas. The effusion method has also been used[3] and the value 222.4 selected for its atomic weight. This agrees with the theory of niton formation, for if an atom of radium with atomic weight 226 is transformed into an atom of niton by the loss of an alpha particle, which is a charged helium atom, then the atomic weight of niton should be four units less than that of radium.

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[1] Ashman, *Am. Jour. Sci.* **26** (iv) 119 (1908).

[2] Gray and Ramsay, *Proc. Roy. Soc.* **84** A, 536 (1911).

[3] Debierne, *Compt. rend.* **150** 1740 (1910) and Perkins, *Amer. Jour. Sci.* **25** (iv) 461 (1908).

Niton is more readily soluble in water than any other of the noble gases. It is also soluble in organic solvents, such as ethyl alcohol, toluene, and amyl alcohol.

The spectrum of niton is the same, whether the discharge is condensed or uncondensed. It resembles the spectra of the other inert gases, each of which contains certain lines whose positions seem to be related to the atomic weight.[1]

Niton is absorbed by cocoanut charcoal at ordinary temperatures, a behavior which is useful both in separation and purification of the element.

Niton emits a characteristic phosphorescence which is so intense in the solid that it is impossible to determine the color in this state. The luminosity is less in the liquid and least in the gas. This phenomenon is supposed to be due to the continuous emission of energy, which is indicated by the evolution of heat as well as the decomposition of water, carbon dioxide, carbon monoxide, ammonia, and hydrochloric acid. Ramsay reports[2] that when niton acts upon solutions of salts of silicon, titanium, zirconium, thorium, and lead, in every case carbon dioxide results. This indicates a breaking down of the larger atoms giving rise to carbon, the simplest atom of the family. The reported change of copper to lithium and water to neon[3] is not regarded as having been definitely demonstrated.[4]

When first separated, niton gas slowly contracts for a day or so, until it occupies about ½ its volume. Then it expands slowly to nearly 3½ times its original volume. At the end of three or four days the spectrum of niton can no longer be detected, but the lines of helium are present. This and other facts of a similar nature have led to the conclusion that niton disintegrates yielding helium.[5] In 3.75 days half the niton has disappeared.

Uses. — Niton is now being used for medical treatments in place of radium. Its use permits a material saving of radium and it is especially useful in small hospitals which are not able to keep on hand a sufficient supply of radium for medicinal use.

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[1] Paul W. Merrill, *Bur. of Standards*, **15** 251 (1919); Science Paper, No. 345.

[2] Ramsay and Usher, *Ber.* **42** 2930 (1909).

[3] Ramsay and Cameron, *Trans. Chem. Soc.* **91** 1604 (1907); **93** 992 (1908).

[4] Rutherford and Royds, *Phil. Mag.* **16** (vi) 812 (1908); also Curie and Gleditsch, *Compt. rend.* **147** 345 (1908).

[5] Ramsay and Soddy, *Proc. Roy. Soc.* **72** 204 (1903); Himstedt and Meyer, *Ann. Physik*, **15** (iv) 184 (1914); Martin, *Chem. News*, **85** 205 (1902).

Is Zero Group Complete?—Although the periodic table seems to justify the conclusion that all the noble gases have been discovered, yet it seems possible that certain strange lines, particularly one at 557, in the spectrum of the aurora may be due to an unknown atmospheric gas. Attempts to separate such a constituent by diffusion through heated quartz and by fractionation of a liquid air residue failed to reveal the presence of any new gas.[1]

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[1] Borel and Jaquerod, *Arch. sci. phys. nat.* **2** 265 (1920).

CHAPTER III

GROUP I — LITHIUM, RUBIDIUM, CAESIUM

LIKE nearly all the other groups in the periodic table, Group I contains two distinct sub-groups called for convenience the A and B divisions. If the relationship between the metals of this group was typical, we would have one so-called typical element, in this case lithium, followed by potassium, rubidium, and caesium in the A division and sodium, copper, silver, and gold in the B division. Obviously sodium belongs with the alkali metals both chemically and physically. On account of the fact that lithium and sodium do not resemble potassium, rubidium, and caesium so closely as these elements resemble each other, it is sometimes considered best to put both lithium and sodium as "typical" elements, introductory to both divisions. It is a very common procedure also to put hydrogen in Group I although it does not harmonize with the other elements. Thus there may be three "typical" elements of this group, although not one of the three is really typical of both divisions. Fig. 4 shows the relationship of the members of this group.

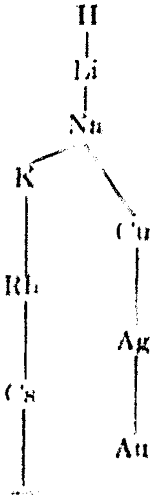

FIG. 4

The typical A division metals, potassium, rubidium, and caesium, resemble each other remarkably. In Division B, copper, silver, and gold are alike in many respects although there are marked differences also. When members of the A division are compared with the metals of the B division, very few resemblances can be found, but the contrasts are so striking that some have preferred to omit copper, silver, and gold from Group I. Mendeleeff was evidently in doubt upon this point, for he put these three elements in both Groups I and VIII. It is doubtful whether the placing of copper, silver, and gold in the same family as the alkali metals is any less logical than putting manganese in the halogen family. A comparison of the A and B divisions of the various groups reveals the fact that very close resemblances are to be observed in groups near the center of the Periodic Table, but as we leave the center in either direction the resemblances grow less marked and contrasts become more noticeable.

The differences between the two divisions of Group I may be summarized as follows: (1) The important, possibly the only, valence in the A division is 1, while the most common valence of copper is 2 and in the most stable compounds of gold the metal has a valence of 3. (2) The alkali metals are the most active metals that we have, standing at the head of the Electromotive Series and displacing all other metals from their combinations. They are easily and quickly oxidized in the air. On the other hand the members of Division B are among the least active of our metals, silver and gold remaining untarnished in the air, while copper oxidizes slowly; these metals are at the foot of the Electromotive Series, being displaced from solutions by nearly all other metals. (3) The alkali metals are never found in anions and they yield no complex cations, while the Division B metals are frequently found in anions such as the important compounds $KAu(CN)_2$ $(K^+ + Au(CN)_2^-)$, $KAg(CN)_2$ $(K^+ + Ag(CN)_2^-)$, $KAuO_2$ $(K^+ + AuO_2^-)$, $KAu(CN)_2$ $(K^+ + Au(CN)_2^-)$. They also appear in complex cations such as $Ag(NH_3)_2Cl$ $(Ag(NH_3)_2^+ + Cl^-)$, $Cu(NH_3)_4(NO_3)_2$ $(Cu(NH_3)_4^{++} + NO_3^-)$. (4) The alkali metals are the strongest base forming elements, as is shown by the facts that their hydroxides are strongly ionized and their halides are not hydrolyzed. The oxides and hydroxides of copper and gold are feebly basic, the latter even at times weakly acidic. The halides of these metals are hydrolyzed, so basic salts are numerous. Silver forms a rather strong oxide, Ag_2O, and its halides are not hydrolyzed extensively. (5) The oxides, sulfides, and chlorides of the alkali metals are soluble in water, while the corresponding salts of copper, silver, and gold are insoluble, with the exception of $AuCl_3$ and $CuCl_2$. (6) The alkali metals occur in nature in combination, the compounds being exceedingly stable. Copper, silver, and gold are found abundantly in the free state. (7) The alkali metals have been discovered within recent times and their uses are largely for scientific purposes. Copper, silver, and gold were among the first metals to be used by primitive man and they have been used since time immemorial as ornaments. They are almost universal and exclusive coin metals.

There are some similarities between Divisions A and B, but they are less striking and not so numerous as the contrasts. The crystal forms of some salts of the two divisions are isomorphous, showing a deep-seated relationship. For example Ag_2SO_4 and Na_2SO_4 display isomorphism, while NaCl, CuCl, and AgCl are also isomorphous. Another relationship between the two divisions is suggested by the fact that the most stable compounds of gold are trivalent and that potassium, rubidium, and caesium probably all form trivalent salts, especially iodides.

Considering the members of Division A, it is easily seen that lithium and sodium differ in many respects from potassium, rubidium, and caesium. Lithium is not a particularly strong alkaline element, while the metallic properties of sodium, potassium, rubidium, and caesium increase gradually as the atomic weight increases. Potassium, rubidium, and caesium form difficultly soluble tartrates and chlorplatinates, and by means of these salts these three elements may be separated from sodium and lithium. The alums of potassium, rubidium, and caesium are also difficultly soluble, while the fluorides of these metals are more readily soluble than those of lithium and sodium. The carbonates of potassium, rubidium, and caesium are deliquescent, while those of lithium and sodium are not. The valence of lithium and sodium is apparently always one, while potassium, rubidium, and caesium form compounds in which the valences may be three or more. The best known of these substances are the iodides, such as the one formed by the solution of iodine in KI. Whether I_2 dissolves in KI forming KI_3 or $KI \cdot I_2$ is a question which cannot be answered finally at present. But the corresponding compound formed by adding iodine to caesium iodine is a stable compound, and caesium di-chloriodide is one of the most stable and most important salts of this metal. The great variety of double salts of caesium would seem to indicate that this element at least sometimes has a higher valence than one.

In comparing the members of the B division with each other, we find them showing resemblances in hardness, occurrence in nature, general activity, and chemical behavior. The color of copper and gold is quite unique among the metals. The insoluble chlorides CuCl, and AgCl are white, and AuCl is nearly so. These metals form similar double salts, such as the cyanides.

It is pointed out forcibly that copper, silver, and gold form transition elements between nickel, palladium, and platinum on the one hand and zinc, cadmium, and mercury on the other hand. It is to be observed from Table VIII that copper, silver, and gold take an intermediate position with respect to fusibility, volatility, coefficient of expansion, and atomic volumes.

TABLE VIII

	MELTING POINT	BOILING POINT	COEFFICIENT OF EXPANSION	ATOMIC VOLUME
Nickel . .	1452.	2340 (30 mm.)	$.0_41516$	6.6
Copper . .	1083.	2310	$.0_4174$	7.1
Zinc . .	419.4	920	$.0_42918$	9.1
Palladium .	1542.	2300	$.0_41280$	9.1
Silver . .	960.5	2100	$.0_41954$	9.2
Cadmium .	320.9	778	$.0_4247$	10.2
Platinum .	1755.	—	$.0_409221$	13.0
Gold . .	1063.	2530	$.0_41451$	10.2
Mercury .	−38.9	357.3	$.0_3182$ Cubical $.0_460$ Approx.	14.7

LITHIUM

Historical. — While working in Berzelius' laboratory in 1817, Aug. Arfvedson discovered in the minerals petalite and spodumene a new alkali element. It differed from the known alkalies in the insolubility of its carbonate, the hygroscopic nature of its chloride and the low melting points of the chloride and sulfate. Because of the fact that this alkali was found in minerals it was given the name lithium, meaning stony, in contrast to sodium and potassium, which are so widely distributed in the plant and animal kingdoms. The work of Bunsen and Kirchhoff with the spectroscope showed[1] that lithium was also very generally distributed among both plants and animals, although usually in small amounts.

Occurrence. — Lithium is found in a considerable number of minerals which are widely distributed over the earth's surface. The three most important sources of lithium in the United States are: (1) Lepidolite, called lithia mica from its appearance, a basic silicate of the theoretical formula $KLi(Al(OH)F)_2 \cdot Al$

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[1] *Phil. Mag.* **20** (iv) 97 (1860).

TABLE IX

Properties of the Alkali Metals

	LITHIUM	SODIUM	POTASSIUM	RUBIDIUM	CAESIUM
Atomic Weight	6.94	23.0	39.1	85.45	132.81
Specific Gravity	0.534	0.9712	0.8621	1.532	1.87
Atomic Volume	13.1	23.7	45.4	55.8	71.0
Melting Point	186°	97°	62.°5	38.°5	26.°5
Boiling Point	1400°	877.°5	700.°	696.°	670.°
Specific Heat	0.941	0.293	0.166	0.0792	0.0482
Color of Flame	Crimson	Yellow	Violet	Red	Blue

$(SiO_3)_3$, containing up to 6 per cent Li_2O, is mined in San Diego County, California. (2) Amblygonite, $AlPO_4 \cdot LiF$, containing 8–10 per cent Li_2O, found in Maine, Connecticut, and especially South Dakota. (3) Spodumene, $LiAl(SiO_3)_2$, containing 4–6 per cent Li_2O, is mined principally in the Black Hills of South Dakota, where it frequently occurs in crystals 30 feet long. In addition lithium is found in varying amounts in a large number of other minerals, in meteorites, spring waters, soils, certain plants such as sugar beet, tobacco, cereals, coffee, and seaweed. It can be detected in milk, blood, muscular tissue, and lungs. Its function in the body is not known.

Mining of lithium minerals in the United States has recently developed rapidly. In 1919 a total of 6287 short tons were produced valued at $115,000. This was more than 10 times as much as was produced in any year preceding 1916. In 1920 the production totaled 11,696 short tons, valued at $173,000. Lepidolite from Pala, California, and spodumene from Keystone, South Dakota, were the chief ores.

Extraction. — From a silicate mineral, lithium compounds may be extracted by long treatment with concentrated HCl. After filtering, Na_2CO_3 is added to precipitate other metals, and the filtrate evaporated to small bulk. Addition of more Na_2CO_3 precipitates Li_2CO_3.

From a phosphate mineral, lithium may be extracted by HCl, with the addition of some HNO_3; the phosphoric acid should be removed by the addition of $FeCl_3$. Evaporate the filtrate to dryness, extract with hot water, add barium sulfide to remove iron, then H_2SO_4 to remove barium. To the filtrate add oxalic acid, evaporate and ignite; the alkali carbonates are formed, of which Li_2CO_3 is the least soluble.[1]

A third method of extraction is described as follows: Finely pulverize the mineral, mix with NH_4Cl and $CaCO_3$, and ignite; extract with water, add HCl and evaporate to dryness, then extract LiCl from the residue with amyl alcohol or pyridine.

Separation. — Lithium may be separated from the other members of the alkali family by the solubility of the chloride in amyl alcohol, pyridine, primary isobutyl alcohol or absolute ethyl alcohol; by the insolubility of the carbonate or of the phosphate in the presence of ammonia and ethyl alcohol; by the solubility of the fluosilicate. Lithium may be separated[2] from sodium by precipitation of NaCl from a solution of the perchlorates in anhydrous n-butyl alcohol by addition of an alcoholic solution of HCl.

Metallurgy. — Arfvedson, Gmelin, and Davy each tried to obtain metallic lithium by electrolysis, and probably each obtained a small amount of the element. But the amounts were so small that little was learned about its properties. So the credit for first studying the metal should go to Bunsen and Matthiessen, who in 1855 used a more powerful current and obtained considerable quantities of the element. They used a bath of fused chloride, but more recently it has been found advisable to add KCl to lower the fusion point of the electrolyte. Kahlenberg has shown[3] that if a current is passed through a solution of LiCl in pyridine the metal is deposited. If LiCl and calcium chips are mixed together and heated in an atmosphere of hydrogen, metallic lithium is obtained.

Properties. — Lithium is a silvery white metal, which tarnishes in the air, though more slowly than any of the other alkali metals. It is a little harder than sodium but softer than lead and is noticeably friable. It can be pressed into wire or welded at room temperature. It is the lightest of all metals, floating upon both water and kerosene.

It reacts with water at ordinary temperature, but the heat of reaction does not melt the metal and is not enough to ignite

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[1] Hugo Müller, *Annalen*, 85 251 (1853).

[2] Willard & Smith, *Jour. Am. Chem. Soc.* 44 2816 (1922).

[3] *Jour. Am. Chem. Soc.* 24 401; *Jour. Physic. Chem.* 3 602 (1899).

the hydrogen even if the water is boiling. When heated in the air, lithium burns quietly with a bright white light, yielding Li_2O, and at red heat it unites readily with hydrogen, forming LiH, which is quite stable. It unites also with nitrogen, forming Li_3N, and burns when heated in chlorine, bromine, iodine, sulfur vapor, or dry carbon dioxide. Dilute sulfuric and hydrochloric acids dissolve the metal readily, but concentrated sulfuric acts more slowly. Nitric acid attacks lithium so violently that the metal usually melts and often ignites.

The metal is rather rare and is usually quoted in one gram lots at a price around $1.50 per gram. It has no commercial use.

In its compounds lithium resembles sodium in that its chloroplatinate is relatively soluble, but the difficult solubility of LiOH, Li_2CO_3, and $Li_3PO_4 \cdot 2\ H_2O$ is in sharp contrast with the behavior of the corresponding salts of the other alkali metals and suggests a close resemblance to magnesium. Li_2CO_3 is decomposed at high temperature, in this respect resembling $MgCO_3$ more closely than the carbonates of the alkali metals.

The lithium atom has been shown[1] to contain two isotopes of atomic weights 6 and 7.

Uses. — Lithium compounds are used in increasing amounts in the manufacture of glass. The chief uses of lithium salts for some years has been in medicine and pyrotechnics.

Compounds. — The compounds of lithium bear a general resemblance to the corresponding compounds of sodium. Nearly all the compounds of lithium are readily soluble in water, the most important exceptions being the carbonate, phosphate, and fluoride. The following are important compounds:

Lithium chloride, LiCl, forms colorless crystals and is one of the most deliquescent salts known. It has a sharp saline taste; is soluble in water, ethyl alcohol, amyl alcohol, ether, chloroform, and pyridine. (See Table X.) When an aqueous solution of LiCl is evaporated to dryness, small amounts of HCl and Li_2O are formed in a manner strongly suggestive of the behavior of $MgCl_2$. It is used in the manufacture of lithia waters and in pyrotechnics.

Lithium hydride, LiH, is formed by direct combination of the elements. Its properties indicate that it is a salt. On electrolysis in a vacuum, hydrogen is liberated from the anode and lithium at the cathode. This is the only instance yet reported in which hydrogen appears to have acid properties and to yield a negatively charged ion.[2]

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[1] Aston, *Nature*, **106** 827 (1921); Dempster, *Phys. Rev.* **18** 415 (1921).

[2] K. Moers, *Z. anorg. chem.* **113** 179 (1920).

TABLE X

Solubilities of Alkali Chloride in 100 g. solvent at 25° C.

	ETHYL ALCOHOL	AMYL ALCOHOL
LiCl	25.8	9.03
NaCl	0.065	0.002
KCl	0.02	0.0008
RbCl	0.078	0.0025

Lithium phosphate is a white crystalline powder which is soluble in acids but difficultly soluble in water.

Lithium carbonate is a white powder, crystalline, whose solubility in water decreases with rise of temperature: at 0°, 100 g. of water dissolve 1.539 g. Li_2CO_3; at 20°, 1.329 g.; at 100°, 0.728 g. It is used in medicine for rheumatism, gout, etc., its value depending on the theory that lithium urate, being more soluble than the sodium salt, should make the elimination of uric acid more complete. Doubt has been raised as to its efficiency for this purpose.

Lithium citrate has a faint alkaline taste and because of its mild taste and non-irritating effect is the most popular lithium salt in medicine. The benzoate, bromide, salicylate, and other salts are also used in medicine for gout, rheumatism, concretions, epilepsy, nephritis, etc.

Lithium hydroxide (or carbonate) is added to the Edison storage battery to increase its capacity. The electrolyte is 21 per cent KOH, and if 50 g. LiOH per liter of electrolyte is added there is produced 12 per cent higher capacity and 21 per cent increase in the electrolyte resistance.

Lithium salts or minerals are sometimes added to the melt in the manufacture of glass on account of the increased fluidity which the lithium produces.

Detection. — Lithium compounds are best detected by the spectroscope. Two lines are prominent, a faint yellow line λ 6104 and a bright red line at λ 6708. As little as a millionth of a milligram may be detected spectroscopically.

RUBIDIUM

Historical. — In 1861, Bunsen and Kirchhoff studied[1] the alkaline constituents extracted from some samples of lepidolite which had been obtained from Saxony. They found that the precipitated potassium chloroplatinate contained a salt somewhat less soluble than itself, whose spectrum contained new lines in the violet, blue, green, yellow, and red. Especially prominent were two red lines lying beyond Fraunhofer's line in the outermost portion of the red solar spectrum. Hence, the name rubidium, dark red, was suggested for the new element. It was present in such small

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[1] *Phil. Mag.* **22** (4) 330 (1861).

amount in the mineral with which Bunsen and Kirchoff were working that they used 150 kilograms of the ore in order to get enough of the new element to study its properties.

Occurrence. — Rubidium occurs widely distributed in nature, always associated with the other alkali elements and usually in very small amounts. Among the minerals, lepidolite contains the largest amount. The mineral from which Bunsen and Kirchoff discovered the element contained 0.24 per cent Rb_2O, though some samples of lepidolite contain as much as 3 per cent of rubidia. Leucite, carnallite, and most lithium ores contain small amounts of rubidium, as do most iron ores, some aluminium ores, and meteorites. Traces are also found in soils, mineral springs, seawater, and seaweed; in beets, tobacco (especially from Havana and Kentucky), coffee, tea, oak, and beech trees. The presence of rubidium in plants seems to be accidental, since neither this element nor lithium can in general replace potassium as a plant food.

Extraction. — Rubidium may be extracted from lepidolite by decomposing the finely ground mineral with calcium fluoride and sulfuric acid; heat, then extract with water, evaporate, and allow the caesium-rubidium alums to crystallize.

Another method may be used to recover rubidium and caesium from any silicate ore. Heat the finely ground mineral with $CaCl_2$ and NH_4Cl, cool, and extract with water. Evaporate, add H_2SO_4, filter off $CaSO_4$, and add $(NH_4)_2CO_3$. Filter and precipitate caesium-rubidium chloroplatinates.

Metallurgy. — Metallic rubidium may be prepared in a variety of ways: (1) electrolysis of the fused chloride, (2) heating RbOH with aluminium or magnesium, (3) heating Rb_2CO_3 with carbon or magnesium, (4) heating RbCl with calcium, (5) heating the tartrate to white heat.

Properties. — Rubidium is a silvery white metal; soft and waxlike even as low as − 10°.0; melts at 38.5°, and boils at 696° giving a bluish vapor. It has greater affinity for oxygen than does potassium, since it takes fire spontaneously in the air, giving an oxide, probably a mixture of Rb_2O and RbO_2. It reacts vigorously with water, yielding RbOH. The atom has two isotopes of atomic weight 85 and 87 which are found in proportion 3 : 1.

Compounds of rubidium resemble those of potassium, with which they are isomorphous. As a rule rubidium salts are more soluble than the corresponding potassium salts. Rubidium shows a characteristic tendency to form complex salts with the halogens, such as $RbIBr_3$, and $RbICl_4$.

The radioactivity of rubidium salts has been studied,[1] but no difference in the intensity of the radioactivity is observable in its salts of various ages. The penetration of the rays from rubidium is found to be intermediate between the Beta rays from UX_1 and radium, the intensity of the rubidium rays being 15 times greater than those from UX_1. The half life period of rubidium is calculated to be 10^{11} years, which is between one-third and one-seventh that of potassium.

There are no commercial uses for rubidium. Its compounds find important use as reagents in microchemistry, where their ready ability to form crystalline compounds makes them of great value in this important and rapidly developing field. It is difficult to buy rubidium material on account of its scarcity. The older catalogues (1911-13) quoted rubidium metal at $1.50-$1.75 per quarter gram and RbCl at 15 cents per gram.

Separation and Detection. — Rubidium and caesium are best separated from the other members of the alkali group by the greater insolubility of their alums, chlorostannates (M_2SnCl_6), or chloroplatinates. (See Table XI.)

TABLE XI

Solubilities of Some Alkali Salts in 100 g. of Water at 17°

$NaAl(SO_4)_2 \cdot 12\ H_2O$	51.0 g.	Na_2PtCl_6	39.77 g.
$KAl(SO_4)_2 \cdot 12\ H_2O$	13.5 g.	K_2PtCl_6	2.17 g.
$RbAl(SO_4)_2 \cdot 12\ H_2O$	2.3 g.	Rb_2PtCl_6	0.20 g.
$CsAl(SO_4)_2 \cdot 12\ H_2O$	0.6 g.	Cs_2PtCl_6	0.18 g.

Rubidium and caesium may be separated from each other by the differences in the solubilities of their alums or chloroplatinates; by the formation of the more stable and less soluble rubidium acid tartrate; by the solubility of Cs_2CO_3 in absolute alcohol; by the formation of the difficultly soluble $CsCl_2I \cdot Cs_2PbCl_6$, or $Cs_3Sb_2Cl_9$.

The quantitative estimation of rubidium may be accomplished by weighing as sulfate, acid sulfate, chloroplatinate, chloride, or perchlorate.[2] Comparison of the intensity of the spectrum lines with those from standard solutions gives a rapid and satisfactory determination of rubidium.[3]

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[1] *Physik. Zeit.* **20** 194 (1919).

[2] Gooch and Blake, *Am. Jour. Sci.* Nov. 1917, p. 381.

[3] Gooch and Phinney, **44** (III) 392 (1892); also *Jour. Ind. and Eng. Chem.* **10** 50 (1918).

CAESIUM

Historical. — In 1846 C. F. Plattner analyzed[1] the mineral pollux or pollucite from the Isle of Elba and was mystified by the fact that the total constituents showed 92.75 per cent. Careful search failed to reveal any error in analysis or any constituents which had been overlooked, and the matter remained a mystery until after the discovery of caesium. In 1864, Pisani repeated[2] the analysis of the same mineral and found that the alkali which Plattner had called potassium was in reality caesium. When corrections are made for the differences in atomic weights Plattner's results are found to be quite accurate. This is a remarkable tribute to Plattner's skill and reliability.

In 1860, Bunsen used the newly devised spectroscope in the examination of the mineral constituents of certain spring waters and discovered two blue lines of unknown origin. He became convinced that they were characteristic of a new alkali metal and he proposed the name caesium, sky blue. This was the first metal discovered by means of the spectroscope, which later revealed the presence of rubidium, thallium, indium, gallium, several of the rare earth group, and all of the noble gases. The discovery of both caesium and rubidium was impossible without the aid of the spectroscope because they are found in such small quantities and their resemblance to potassium is so striking that the ordinary methods of analysis are not effective. The sensitiveness of Bunsen's spectroscope is shown by the fact that the water from which the caesium lines were first obtained did not contain more than 2 or 3 grams per ton, and he was compelled to evaporate 40 tons of the water in order to obtain enough caesium for study.

Occurrence. — Caesium is widely distributed in nature almost always with the other alkalies and usually in very small amounts. The mineral pollux or pollucite, essentially $H_2O \cdot 2\,Cs_2O \cdot 2\,Al_2O_3 \cdot 9\,SiO_2$, occurs sparingly on the Isle of Elba and in Maine. It contains about 34 per cent Cs_2O. Caesium is also found in small amounts in other minerals such as lepidolite and beryl; in mineral waters, where it is almost always associated with large amounts of the other alkalies. It is also found in traces in many soils, but only a few plants, such as tobacco, absorb it.

In the absence of potassium, caesium is a poison for most forms of plant life.

Extraction; Separation; Detection. — See Rubidium.

Metallurgy. — Metallic caesium was first prepared in 1881 by Setterberg, who used the electrolysis of a mixture of CsCN and $Ba(CN)_2$. The metal may also be prepared by reducing CsOH with aluminium or magnesium; by heating Cs_2CO_3 with magnesium or CsCl with calcium.

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[1] Pogg. *Ann.* **69** 443 (1864).

[2] *Compt. rend.* **60** 714 (1865).

Properties. — Caesium is a silvery white metal when pure, but it is frequently golden yellow due to the presence of a small amount of oxide or nitride. It is one of the softest of the metals, its melting point being about 26.°5. It is the most electro-positive of all the metals. On exposure to air it gradually melts owing to the lowering of its melting point by the impurities formed in contact with the air. It finally bursts into flame, producing the oxide. When thrown upon water it floats in spite of its high specific gravity (1.87) and burns with reddish-violet flame.

Caesium and its compounds are more rare than rubidium. Salts of caesium are used as reagents in microchemistry. The metal was quoted (1911–13) at $1.75 to $2.25 per quarter gram and the chloride at 30 cents per gram, but the material is difficult to obtain at almost any price.

Does Eka-caesium exist? — Several considerations point to the possibility of the existence of an undiscovered alkali element, with atomic number 87 and an atomic weight of approximately 224. Diligent search in caesium materials has been made[1] for this missing element by fractionation of the nitrate, dichloriodide, chloride, perchlorate, sulfate, and alums. In every case careful examination of the extreme portions of the material failed to reveal any indication of a new element. If such an element exists, it must belong very definitely to the radioactive series and it may have such a short life period that its detection becomes very difficult.

Harkins[2] points out that of the known elements bismuth has the highest odd atomic number (83) except the radioactive descendants of uranium or thorium, whose half life periods, so far as they are known, are very short. The even atomic numbers from 82 to 92 are represented fully and many of these elements are very stable. It seems reasonable, therefore, to conclude that the electron systems required for the atomic numbers 85 and 87 are unstable and may not be able to exist at all.

Compounds of Group I. — There is a general resemblance between the compounds of the elements of the alkali group. The chief distinctive features of the compounds of lithium, rubidium, and caesium have already

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[1] See Richards and Archibald, *Proc. Am. Acad.* **38** 449 (1903); Gregory P. Baxter, *Jour. Am. Chem. Soc.* **37** 286 (1915) and Dennis and Wyckoff. *ibid.* **42** 985 (1920).

[2] *Jour. Am. Chem. Soc.* **42** 1985 (1920).

been pointed out. The principal compounds of the group may be briefly summarized as follows: —

All members of the group form several oxides and a surprising amount of uncertainty exists concerning them. They probably all form the simple oxide M_2O by direct union of the elements, but there is some doubt in the case of rubidium. These oxides react with water forming the characteristic bases MOH, whose strength increases with increase in atomic weight.

Peroxides of the formula M_2O_2 are important in the case of each element of the family except potassium, and K_2O_2 may not even exist.

Oxides of the formula M_2O_3 are reported in the case of all the elements of the family except lithium and potassium.

M_2O_4 or MO_2 are important oxides of potassium, rubidium, and caesium, but an oxide of this composition has not been recognized in the case of lithium and sodium.

In addition to the oxides already enumerated the following irregular oxides are mentioned: Na_3O, K_4O, K_8O_6, K_6O_4, K_4O_3. Their existence is quite uncertain.

All form carbonates M_2CO_3 and bicarbonates $MHCO_3$.

All form the hydride[1] MH by direct union of the elements at somewhat elevated temperatures; the hydrides with water give $MOH + H_2$; the rubidium and caesium hydrides are unstable at ordinary temperatures.

The alkali metals are capable of forming nitrides of the formula M_3N as well as azoimides of the formula MN_3. The latter are best considered as salts of hydrazoic (triazoic) acid, N_3H. All metals of this group form amino compounds such as MNH_2; metal ammoniums like MNH_3 are also characteristic.

Each member of the family forms the simple salt with each of the halogens. Potassium, rubidium, caesium, also form polyhalides like KI_3, $KICl_4$, in which the valence of the metals appears to be 3 or 5. Abegg mentions CsI_9, and Wells and Wheeler[2] describe a lithium compound of the formula $LiICl_4 \cdot 4\,H_2O$. Caesium forms complex chlorides with gold, silver, zinc, copper and mercury such as $CsAuCl_4$, $Cs_4Ag_2Au_2Cl_{12}$, $Cs_4ZnAu_2Cl_{12}$, etc.

Chlorates, perchlorates, bromates, and iodates are important compounds.

Carbides, M_2C_2, have been prepared for the first three members of the family. The carbides react with water, giving C_2H_2 and MOH.

Sulfur, phosphorus, and silicon form many compounds of the familiar types.

[1] Moissan, *Compt. rend.* **136** 587 (1903).

[2] *Zeit. anorg. Chem.* **2** 255 (1892).

CHAPTER IV

GROUP II — RADIUM, RADIOACTIVITY, MESOTHORIUM

THE elements which are found in Group II of the periodic table are easily divided into the A division including calcium, strontium, barium, and radium and the B division including zinc, cadmium, and mercury. This leaves both beryllium and magnesium as introductory or "typical" elements. The relationship is shown in Fig. 5. All the members of this group are characteristically bivalent; in fact two is almost the only valence shown. The most important exception to this statement is in the case of the mercurous compounds, but it has been suggested that this exception is more apparent than real, since in the mercurous compounds we have reason to believe that the mercury atoms are in groups of two whose valence is two. Hence, Hg_2Cl_2 not HgCl. The alkaline earth metals form monovalent compounds with the halogens, but these are obscure and somewhat doubtful.

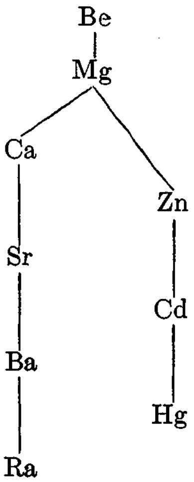

FIG. 5

All the members of this group form oxides of the type MO and basic compounds $M(OH)_2$. The latter are soluble in the case of A division metals and difficultly soluble in B division metals.

The only elements of this group which may fairly be considered rare are beryllium, radium, and mesothorium. The first named belongs distinctively to the B division and is discussed in Chapter V. The present chapter is devoted to radium and mesothorium, with a brief discussion of the phenomena of radioactivity.

The metals of Division A are designated as alkaline earths because they are intermediate between the alkali metals of Group I and the "earths" of Group III. These metals oxidize readily in the air and decompose water at ordinary temperatures, liberating hydrogen. The oxides are markedly basic, with very high fusion points and such great stability that they were regarded as elements until 1807, when Davy showed them to be compounds of a metal and oxygen. They possess striking affinity for water, with which they combine to form hydroxides, the solubilities of which increase with increasing atomic weight of the metal. They also form peroxides, MO_2, hydrides, and nitrides. The carbonates, chromates, phosphates, sulfates, and salts of many organic acids are difficultly soluble in water.

Radium is classed with the alkaline earth metals with which it properly belongs, although it shows some decided peculiarities. It is to be observed that in nearly every case that member of a family which falls in the last series of the periodic table has certain marked peculiarities. The physical properties of the members of this family are shown in Table XII.

TABLE XII

Properties of the Alkaline Earth Metals

	CALCIUM	STRONTIUM	BARIUM	RADIUM
Atomic Weight	40.07	87.63	137.37	226.0
Specific Gravity	1.52	2.55	3.75	
Atomic Volume	26.4	38.7	36.5	About 30
Specific Heat	0.152		0.068	
Melting Point	780°	800°	850°	About 700°
Heat of Formation of MO in Cal.	131.3	130.98	130.38	
Absolute Electric Potential	2.4	2.6	2.6	

RADIUM AND RADIOACTIVITY[1]

Historical. — The phenomenon of radioactivity was discovered by Henri Becquerel in 1896, who observed that the salts of uranium emit radiations which are capable of reducing the silver salts of a photographic plate even when it is securely wrapped in black paper. This property was found to be char-

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[1] See R. A. Millikan, Curie address on "The Significance of Radium," *Sci.* July 1, 1921, page 1, the address delivered at the presentation of the Willard Gibbs Medal to Mme. Curie; *Chem. and Met. Eng.* **24** 1132 (1921); Russell, *The Chemistry of the Radioactive Substances*, Macmillan (1922).

acteristic of uranium whether it was in the form of the element or of any of its compounds. Becquerel also found that uranium had the power to discharge an electroscope and that the rate of discharge is an accurate measure of the amount of radioactive substance present.

In studying the radioactivity of certain uranium minerals, P. and S. Curie found that the pitchblende residues from St. Joachimsthal, Bohemia, were more than three times as radioactive as uranium itself. This fact suggested the presence of a powerfully radioactive substance, and led to a thorough examination of the residues.

Pitchblende is one of the most fertile sources of radioactive material. Its composition varies widely, but it always contains an oxide of uranium, associated with oxides of other metals, especially copper, silver, and bismuth; the Austrian mineral contains cobalt and nickel; the American samples contain no cobalt or nickel but are largely associated with iron pyrites and arsenic; zinc, manganese, and the rare earths are frequently present, while occasionally calcium, barium, aluminium, zirconium, thorium, columbium, and tantalum are reported. Dissolved gases, especially nitrogen and helium, are present in small proportions.

From this mineral it was formerly customary to extract the uranium and discard the residue. The chemical study of such a complex mixture is an exceedingly difficult task, but by patient effort M. and Mme. Curie succeeded[1] in 1898 in separating two new radioactive substances to which the names radium and polonium were applied. The latter is now commonly called radium F. Later Debierne discovered[2] a third radioactive constituent of pitchblende residues and named the new substance actinium.

The method of treatment consisted in effecting a concentration of some of the constituents of the residues and observing the radioactivity of the various portions into which the material was divided. It was observed that if barium was concentrated the radioactivity of that portion increased rapidly. From a ton of residues there may be prepared 10–20 kilograms of crude sulfate whose activity is about 60 times that of uranium. The Curies then converted the sulfates to chlorides and subjected the material to the process of fractional crystallization. After a number of crystallizations there was obtained in the most insoluble portion a fraction of a gram of radium chloride which was a million times as active as uranium. One ton of pitchblende is said to contain 0.37 gram of radium, 0.00004 gram of polonium,[3] and a small amount of aetinium.

In 1902, Geoffrey Martin suggested[4] that radioactive elements were gradually undergoing decomposition. This theory was greeted with ridi-

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[1] See *Chem. News*, 1903, for translation of thesis.

[2] *Compt. rend.* **129** 593 (1899); **130** 906 (1900); **136** 446, 767 (1903).

[3] Marchwald obtained 3 milligrams of polonium from 15 tons of pitchblende.

[4] *Chem. News*, **85** 205 (1902).

cule at first, but within a year Rutherford and Soddy adopted this view and soon established it firmly through their epoch-making investigations. Radium emanation was first recognized as a gas in 1902 by Rutherford and Soddy. The revolutionary fact that helium results from the disintegration of radium atoms was first demonstrated by Ramsay and Soddy in 1903. The position of the radioactive elements in the periodic table was established by the combined work of Fajans, Russell, Fleck, and Soddy in the years 1913–15, through the development of the conception of isotopes.

Occurrence. — Radium is widely distributed in nature, never in very concentrated form and usually in exceedingly minute quantities. The principal source of radium until recently was the Bohemian pitchblende from which radium was first extracted. This is still the most important source of radium in Europe, but the carnotite ores of Colorado now produce a considerable proportion of the world's radium supply.

All uranium ores contain radium and consequently may serve as a source of radium. Torbernite, a hydrated copper uranium phosphate, and autunite, a hydrated calcium uranium phosphate, are found in Portugal and Australia, from which considerable radium has been extracted. There are apparently extensive deposits of low grade torbernite and autunite in New Mexico.

In addition to its distribution in minute amounts in many rocks and minerals, radium is found in many mineral springs[1] and in seawater.

Mining and Concentration of Carnotite.[2] — Since carnotite is the world's most important source of radium, much interest attaches to its production. The main deposits now known are in the southwestern part of Colorado and extending over into Utah. The deposits are scattering, varying greatly in thickness, extent, and purity of the ore. The carnotite is usually deposited in sandstone, upon which it forms amorphous incrustations replacing the original cement. The color of the high-grade carnotite is a rich canary yellow, the lower grades having various shades of yellow, orange, brown, green, or black. The ore frequently crops out along the cliffs or canyon walls, and even if the outcrop is low-grade ore it may lead to a pocket of rich ore.

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[1] Skinner and Sale, "Radioactivity of Water," *Jour. Ind. and Eng. Chem.* 14 949 (1922).

[2] See Bureau of Mines *Bulletin*, 103 (1917).

In some localities open mining is used; in the gulleys small tunnels are commonly used and occasionally shallow shafts are sunk. The ore is loosened by blasting, and sorted into waste, low grade or milling ore, and high grade shipping ore. The sorting is a difficult matter and requires long experience and keen judgment. Doubtful specimens are tested with an electroscope for their uranium content. The high grade ore is placed in small canvas sacks, in order to save the fine portions, which are frequently very rich material.

The low grade ore, which contains about 0.8 per cent U_3O_8, is sent to the concentrating mills, where it is concentrated to about 3 per cent U_3O_8. The concentration of the carnotite involves the separation of the binder from the grains of sand. This is done by coarse grinding (80–100 mesh) and separation of the fine particles by either the dry or wet process. In the dry method the ground ore is run through a special attrition apparatus whose function is to rub off the carnotite adhering to the grains of sand. Then the fine particles are removed by suction. In the wet method of concentration, the ground ore is elutriated to remove as much adhering carnotite as possible. Then the material is thoroughly agitated with water and allowed to settle. Finally the slimes are drawn off and the process repeated as long as necessary.

Extraction.[1] — Many methods have been proposed for treating carnotite ores; they are of three general types — those using (1) an acid leach, (2) an alkaline leach, or (3) fusion methods. Of the acid methods the following are used: (*a*) Hot strong sulfuric acid dissolves from the ore uranium, vanadium, copper, barium, and radium; when the extract is diluted to 10 per cent free acid the impure radium-barium sulfate precipitates. The precipitate may be boiled with Na_2CO_3 and the radium-barium leached out with HCl. This method requires much labor and the cost is high. (*b*) Hydrochloric acid leaches out the radium and barium, which are precipitated by partially neutralizing the acid and adding a sulfate.[2] The acid used should be prac-

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[1] See "Extraction and Recovery of Radium, Uranium, and Vanadium from Carnotite," *Bulletin* 104, Bureau of Mines; also H. D. d'Aguiar, "Radium Production in America," *Chem. and Met. Eng.* **25** 825, 877 (1921) and the comments on the latter by S. C. Lind, *ibid.* **26** 1012 (1922).

[2] See F. E. E. Germann, "Adsorption of Radium by $BaSO_4$," *Jour. Am. Chem. Soc.* **43** 615 (1921).

tically free from sulfuric acid. This method will give an 80–90 per cent extraction if the ore is free from sulfates; but since gypsum is frequently found in carnotite ores the extraction in some ores is as low as 40–50 per cent. (c) The Bureau of Mines recommends the use of nitric acid, which dissolves practically all valuable constituents of the ore. The excess acid is neutralized by NaOH and then $BaCl_2$ and H_2SO_4 are added. The sulfates are reduced with carbon, dissolved in HCl, and the radium-barium chlorides subjected to fractional crystallization. This method extracts 90 per cent of the radium, nearly all the uranium, but leaves considerable vanadium in the residue. The cost of the acid would be prohibitive, except for the fact that $NaNO_3$ is crystallized from the final liquors. In this way the actual consumption of nitric acid is small. The great advantage claimed for the nitric acid method is the efficiency in the recovery of radium.

In the methods using an alkaline leach the ore is boiled either with sodium carbonate which extracts a considerable portion of both vanadium and uranium, or with sodium hydroxide which removes vanadium only. Radium may then be extracted with HCl, after which the remaining uranium and vanadium may be reclaimed. This method extracts the valuable constituents of the ore, but much difficulty is experienced in filtering the HCl solution because the liberated silicic acid clogs the filtering medium.

Two general fusion methods are used: (*a*) Fusion with sodium sulfate, used by the Austrian Government in treating pitchblende ores, but cannot be used with American carnotite. (*b*) Fusion with Na_2CO_3 brings the uranium, vanadium, and silica into soluble form. From the insoluble residue HCl extracts the radium and barium in the form of chlorides.

As the richer ores become more and more difficult to obtain greater attention is naturally directed to extraction methods which are efficient in dealing with low grade ores. A method[1] which is said to give 83 per cent extraction from carnotite or autunite containing no more than 5.0×10^{-7} per cent of radium, consists in sintering the ore with NaCl or $CaCl_2$ with the addition of $CaCO_3$. After cooling, the mixture is ground coarsely and leached with HCl; then H_2SO_4 and $BaCl_2$ are added. The

[1] Ebler und Van Rhyn, *Z. angew. Chem.* **34** 477 (1921).

radium-barium sulfate is obtained as a milky suspension free from quartz, thereby reducing the bulk of the material to 7 per cent of the original ore.

The recovery of radium from luminous paints is possible[1] by dissolving the radium salts and precipitating radium-barium sulfate in the usual way. The loss during recovery is about 1 per cent.

Purification. — The extraction methods yield a mixture of radium and barium chlorides or sulfates. If sulfates are obtained, they are reduced to the sulfides by mixing with charcoal and heating to about 800°; or changed to carbonates by boiling with Na_2CO_3.

The sulfides or carbonates are ground dissolved in HCl and the chlorides subjected to fractional crystallization. Radium chloride is less soluble than barium chloride and consequently the former collects in the less soluble portion of the series. Other impurities, such as iron, aluminium, and vanadium, also collect at the soluble end and consequently give no trouble in radium concentration. Lead if present is particularly troublesome. Some lead is removed as chloride and some as sulfide, but the solubility of these salts and of the sulfochloride, $(PbS)_x \cdot PbCl_2$, in acid prevents its complete removal from strongly acid solution. It is completely removed by making the fractions alkaline with ammonia and saturating with H_2S. The loss of radium during this operation has been shown to be not over 0.2 per cent.

After fractionating for a time as chloride, it is found advantageous to continue the process as bromides, which produces a more rapid concentration of radium.[2] The conversion to bromides is accomplished by precipitating the radium and barium with ammonium carbonate and dissolving the precipitate in hydrobromic acid. Crystallization of the bromides is best carried out in silica ware. After 10-12 crystallizations as bromide the least soluble fraction, which should contain 1-4 per cent radium bromide, is thoroughly dried and sealed in a glass tube. The radium content may be determined by the gamma ray measurement.

After obtaining a number of tubes in this manner, their

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[1] A. G. Francis, *J. Soc. Chem. Ind.* **41** 94 (1922).

[2] C. E. Scholl, *Jour. Am. Chem. Soc.* **42** 889 (1920).

contents are put together and the higher fractionation carried out in the same manner. By a repetition of this process, radium material of a high degree of purity may be obtained.

Various modifications of these methods have been made, such as the fractionation of the hydroxides[1] and of the iodides.[2]

Supply of Radium. — It is estimated that the total amount of extracted radium in the world is about 5 ounces. To this supply there is being added, during normal times, roughly about an ounce each year. But since the production of this amount of radium requires the mining of about 6000 tons of ore, serious concern has been felt for the future supply of this element. The deposits of Europe are already showing signs of exhaustion, and the Bureau of Mines estimates that the Colorado ore now in sight will not produce more than 180 grams of radium. Others are more optimistic and place the total yield of the Colorado deposits as high as 900 grams of the element. It is worthy of note also that new deposits are being discovered and it is quite possible that new supplies of ore and more efficient methods of extraction will cause the output to increase rather than decrease. Careful economy in the use of radium is necessary in spite of the most optimistic reports, however.

During the war the increased demand for radium stimulated production enormously. With the signing of the armistice there came a greatly decreased demand, consequently radium production slowed up considerably, until the stock on hand was used up. Toward the close of 1919 the radium industry revived appreciably and during 1920 the total production of radium amounted to approximately 35 grams of the element.[3] This is the largest output of any year and is only slightly less than the total produced up to date from European ores.

New deposits of uranium-radium ores are reported from Lusk, Wyoming, in Grant County, New Mexico, and near Georgian Bay, Ont.[4] The former is being developed, yielding an ore containing up to 1.5 per cent U_3O_8. A new deposit of rich radium-uranium ore is reported at Jachymov, Bohemia, which is said to contain sufficient ore for 20 years. A large

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[1] McCoy, *U. S. Pat.* 1,103,600, July 14, 1914.

[2] Hopkins and Rudde, *Sch. Sci. and Math.* **22** 752 (1922); *Proc. Ill. State Acad. of Sci.* 1921.

[3] R. B. Moore, *Eng. and Min. Jour.* **111** 151 (1921).

[4] *Ann. Report Ont. Bur. Mines*, **28** 94.

and particularly rich deposit of pitchblende has recently been discovered at Katanga, Belgian Congo.[1]

The price of carnotite ore is considerably higher than two or three years ago, not only on account of increased demand for radium, but also because of the steadily growing demand for vanadium in the steel trade. The steel industry is also showing increasing interest in uranium.

The price of radium has shown considerable fluctuation within the past few years. During the war radium salts of high grade, with a purity of 50 per cent or better, sold as high as $125 per milligram of the element. During the early spring of 1920 one sale of over 2 grams was made at $89,000 per gram of element. Later in the year the price rose to $110–$120 per milligram, with a slowly rising market. In December, 1922, the price had fallen to $70.00 per milligram owing to the rich deposits in the Belgian Congo.

Metallurgy. — Metallic radium was prepared by Mme. Curie and Debierne[2] by the electrolysis of radium chloride, using a platinum-iridium anode and a mercury cathode. The radium was collected as an amalgam which was heated in an atmosphere of hydrogen until the mercury was distilled off. Its properties have not all been determined. It is to be expected that the metallurgy of radium would present particular difficulties, not only on account of the scarcity of the material and difficulties in preparing its pure salts, but also on account of the fact that the difficulties in reduction of the alkaline earth metals increase with atomic weight. Metallic calcium is expensive, metallic strontium is rare, and pure metallic barium has never been prepared. Consequently, the production of any metallic radium is a distinct triumph.

Properties. — Radium is a white metal, with a melting point of about 700°. It blackens rapidly in the air due to the formation of the nitride. It chars paper, and reacts readily with water, forming the hydroxide. It dissolves easily in HCl. The element displays all the phenomena of radioactivity which are characteristic of its salts. On this account it is customary to speak of the amount of radium element present in a compound

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[1] One ton of ore is said to contain 120 mg. of radium; *Bull. soc. chim. belg.* **30** 219 (1921).

[2] *Compt. rend.* **151** 523 (1910).

and disregard the presence of the elements with which it is in combination.

In addition to the properties which relate radium to the alkaline earth metals, it is distinguished from them strikingly by possessing the properties of a radioactive substance. This means that both the element and its compounds continuously emit the penetrating rays which Becquerel observed first in substances containing uranium. The emission of these rays is a permanent and abiding property of radioactive atoms and the radiation is independent of light, temperature, pressure, and all other physical conditions. No indication of change in the rate of radiation has been detected, although the phenomena have been observed between temperatures of 2000° and −250° C. Since all purely chemical phenomena are influenced by physical conditions, it is necessary to conclude that radioactivity is not an ordinary chemical phenomenon, but is due to changes within the atom itself. These intra-atomic changes are possible because of the very complex nature of the radioactive atoms and are caused by the fact that within a given interval of time a definite proportion of the atoms breaks up or disintegrates, with the expulsion of radioactive influences. It is now recognized that the seat of the explosion which results in disintegration of the atom is in the nucleus, but the cause is unknown. In a given interval of time a definite proportion of the atoms of a radioactive element explodes, expelling part of the original atom and leaving behind an atom with new properties.

In addition to the influence on the photographic plate and the discharge of the electroscope, radioactive substances have certain very striking effects. They render diamonds, rubies, fluorspar, and zinc sulfide brilliantly phosphorescent. They produce severe burns on the flesh and kill lower animals; they coagulate proteid; transform oxygen into ozone; form hydrogen peroxide, and decompose water slowly but continuously; they change yellow phosphorus into red; reduce mercuric salts to mercurous, and ferric to ferrous; they decompose iodoform, potassium bromide, hydrogen sulfide, carbon dioxide, and other compounds.

Three distinct types of radiations are recognized. The *Alpha* particles are positively charged, are projected at varying velocities from different atoms, but of the order of $\frac{1}{10}$ the velocity of light. They have low penetrating power, so never travel far from their source, but they are the main cause of phosphorescence. They have a mass of four and are known to be helium atoms each carrying two positive charges of electricity. They comprise about 90 per cent of the radiation from radium. They are distinguished by the following characteristics: They are absorbed by 10 cm. of air or 0.1 mm. of metallic aluminium; they show a positive deflection in a magnetic field; they produce ionization of a gas, and affect a bare photographic plate quite strongly, though their low penetrating power does not enable them to affect a plate which is wrapped in paper. The *Beta* particles are negatively charged and are shot off at velocities varying from 20 to 99 per cent of the velocity of light. They correspond to the cathode rays which are produced by a vacuum tube discharge, and are considered streams of negatively charged electrons. Their smaller size and higher velocity give them greater penetrating power than the alpha particles. They are able to penetrate as much as three millimeters of aluminium. They comprise about nine per cent of the radium radiations. They are distinguished from the other forms of radiation by the fact that they are absorbed in a thick sheet of aluminium, that they show a marked negative deflection in the magnetic field, that they are highly effective in producing ionization, fluorescence, and photographic effects. The *Gamma* radiations differ from the alpha and beta in that they are not influenced by a powerful magnetic field. They have tremendous penetrating power, as they have been known to pass through 20 centimeters of lead. Since a solid has the power of absorbing gamma rays in direct proportion to its density, a sheet of aluminium must be five times as thick as lead in order to produce the same absorption. The gamma rays are *not* material substance at all, but pulsations similar to Röntgen rays. They are vibrations of very short wave length.

Thus it is seen that a radioactive substance is continuously emitting a tremendous amount of energy. One gram of radium evolves energy equivalent to 118 calories per hour — more than enough to raise its own weight of water from 0° to 100°. During the half life period this represents 250,000 times as much energy as is obtainable by burning an equal weight of coal.

At the present time there are recognized about 35 distinctly different elements which emit radiations. At first it was difficult to locate so many elements in the periodic system, but the difficulty was solved when it was recognized that atomic numbers, not atomic weights, are the fundamental characteristics of the elements. So the theory of isotopes explains how several elements may occupy the same position in the periodic table.

These radioactive elements differ among themselves both in the rate at which they emit radiations and in the type of radiation. Some elements emit alpha rays only, others emit beta rays, while a few elements appear to emit both. Since both the alpha and beta rays are made up of electrons, it is evident that when an atom loses either an alpha or a beta particle the residue is different from the mother atom. If an alpha particle is lost, the atomic weight is decreased by 4 and the residue must take a position in the periodic table two spaces to the left. If a beta particle is lost the atomic weight is not appreciably changed, but the loss of an electron changes the chemical nature of the residue, which moves one space to the right but retains its former atomic weight. Thus the disintegration of the parent element produces a radioactive element which becomes in turn the parent of another product. So a whole series of elements arises from a single primary radioactive body. Three such series are recognized, usually called the uranium, thorium, and actinium series. There is reason for believing that the actinium series is in some way related to uranium, probably through a branch chain from uranium II. (See Table XIII *B*.) Both uranium and thorium are considered primary radio elements, since neither is the product of the disintegration of any known element.

The relationship between the members of these series may be better understood by studying a few members of one of the series. Uranium, the parent substance of its series, has an atomic weight 238, but its atoms are not permanently stable. In any second of time one atom out of each 10^{18} explodes and emits an alpha particle which is a charged helium atom. The residue accordingly has an atomic weight 234, and its properties show that it is a different element. This substance is called uranium X_1, and its chemical properties are identical with those of thorium, from which it differs in mass alone.

TABLE XIII[1]

A — The Uranium Series

UI(238) **4.67×10^9 years** **Primary body**	$\xrightarrow{\alpha}$	UX$_1$(234) 24.6 days Thorium	$\xrightarrow{\beta}$	UX$_2$(234) 1.15 minutes Protoactinium	$\xrightarrow{\beta(\gamma)}$	UII(234) 2×10^6 years Uranium	$\xrightarrow{\alpha}$	Io(230) 6.9×10^4 years Thorium	$\xrightarrow{\alpha}$
Ra(226) **1690 years** **Mesothorium 1**	$\xrightarrow{\alpha(\beta\gamma)}$	Rn(222) 3.85 days Thoron	$\xrightarrow{\alpha}$	RaA(218) 3 minutes Polonium	$\xrightarrow{\alpha}$	RaB(214) 26.8 minutes Lead	$\xrightarrow{\beta(\gamma)}$	RaC(214) 19.5 minutes Bismuth	$\xrightarrow{\beta\gamma}$
RaC′(214) **10^{-6} seconds** **Polonium**	$\xrightarrow{\alpha}$	RaD(210) 16.5 years Lead	$\xrightarrow{(\beta\gamma)}$	RaE(210) 5 days Bismuth	$\xrightarrow{\beta}$	RaF(Po)(210) 136 days Polonium	$\xrightarrow{\alpha\gamma}$	RaΩ′(206) Stable Lead	

B — The Actinium Series

U(92)	$\xrightarrow{\alpha}$	**UY(90)** **104 days** **Thorium**	$\xrightarrow{\beta}$	Pa(91) 12,000 years UX$_2$	$\xrightarrow{\alpha}$	Ac(89) 20 years MesoTh2	$\longrightarrow$	RdAc(90) 19.5 days Thorium	$\xrightarrow{\alpha(\beta)}$	AcX(88) 11.4 days Radium	$\xrightarrow{\alpha}$	An(86) 2.9 seconds Radon	$\xrightarrow{\alpha}$
				AcA(84) 0.002 second Polonium	$\xrightarrow{\alpha}$	AcB(82) 36.1 minutes Lead	$\xrightarrow{\beta(\gamma)}$	AcC(83) 2.15 minutes Bismuth	$\xrightarrow{\alpha}$	AcC″(81) 4.71 minutes Thallium	$\xrightarrow{\beta\gamma}$	AcΩ″(82) Stable Lead	

C — The Thorium Series

Th(232) **1.31×10^{10} years** **Ionium**	$\xrightarrow{\alpha}$	MsTh1(228) 6.7 years Radium	$\longrightarrow$	MsTh2(228) 6.2 hours Actinium	$\xrightarrow{\beta\gamma}$	RdTh(228) 2.02 years Thorium	$\xrightarrow{\alpha\beta}$	ThX(224) 3.64 days Radium	$\xrightarrow{\alpha}$
Tn(220) **54 seconds** **Radon**	$\xrightarrow{\alpha}$	ThA(216) 0.14 second Polonium	$\xrightarrow{\alpha}$	ThB(212) 10.6 hours Lead	$\xrightarrow{\beta\gamma}$	ThC(212) 60 minutes Bismuth	$\xrightarrow{\beta}$	ThC'(212) 10^{-11} seconds Polonium	$\xrightarrow{\alpha}$
ThΩ'(208) **Stable** **Lead**									

D — The Branch Series

$$\begin{tikzcd}
 & \text{RaC}'(214) \arrow[r, "\alpha"] & \text{Uranium Series} \\
\text{RaC} \arrow[ur, "99.97\%\ \beta"] \arrow[dr, "0.03\%\ \alpha"'] & & \\
 & \begin{array}{c}\text{RaC}''(210)\\ \text{1.4 minutes}\\ \text{Thallium}\end{array} \arrow[r, "\beta"] & \begin{array}{c}\text{RaΩ}''(210)\\ \text{Stable}\\ \text{Lead}\end{array}
\end{tikzcd}$$

$$\begin{tikzcd}
 & \text{ThC}'(212) \arrow[r, "\alpha"] & \text{ThΩ}'(208) \\
\text{ThC} \arrow[ur, "65\%\ \beta"] \arrow[dr, "35\%\ \alpha"'] & & \\
 & \begin{array}{c}\text{ThC}''(208)\\ \text{3.1 minutes}\\ \text{Thallium}\end{array} \arrow[r, "\beta\gamma"] & \begin{array}{c}\text{ThΩ}''(208)\\ \text{Stable}\\ \text{Lead}\end{array}
\end{tikzcd}$$

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[1] This table conforms with the recommendations of the International Committee on Chemical Elements. See Jour. Am. Chem. Soc. 45 867 (April, 1923).

The atoms of uranium X_1 are likewise unstable, and during each second one atom in every 10^7 disintegrates, expelling a beta particle. This forms other new atoms which have the same mass as those of uranium X_1, but differ from them in chemical behavior. These new atoms comprise the element uranium X_2. But the atoms of this element represent a very unstable form and one atom per hundred explodes each second, liberating another beta particle and forming atoms of the element uranium II, an isobar of uranium X_1, and uranium X_2, and an isotope of the parent, uranium. Uranium II loses an alpha particle, producing ionium, of atomic weight 230, isotope of uranium X_1. This process continues until a stable atomic structure is reached, when the series ends.

If the atoms of the radioactive elements continue to "shoot themselves to pieces" by throwing out radiations and forming new elements, it is evident that in time any given sample of an element will disappear. Since the rate of radiation differs in different elements it is evident also that some elements will disappear more quickly than others. The rate of disintegration for the various elements has been studied and is usually expressed in the time required for any sample of an element to disintegrate to half value. This is called the half life period. Table XIII shows the three disintegration series, the atomic weight of each element,[1] the radiation which it emits, the half life period and the most common substance which is isotopic with the product. The atomic weights shown in heavy type have been determined experimentally.

Table XIV shows the position in the periodic table of the principal members of the three series. By starting with the parent element of each series and following the dotted arrows it is possible to trace the series through to the end. Atomic weights are shown under each symbol and the atomic number of each group of isotopes is given in parenthesis.

In several places in these series an unstable arrangement seems to give two disintegration products, due to the fact that some atoms expel an alpha particle while at the same time other atoms give off a beta particle. This gives rise to the branch series, the more important of which are shown in Table XIII *D*.

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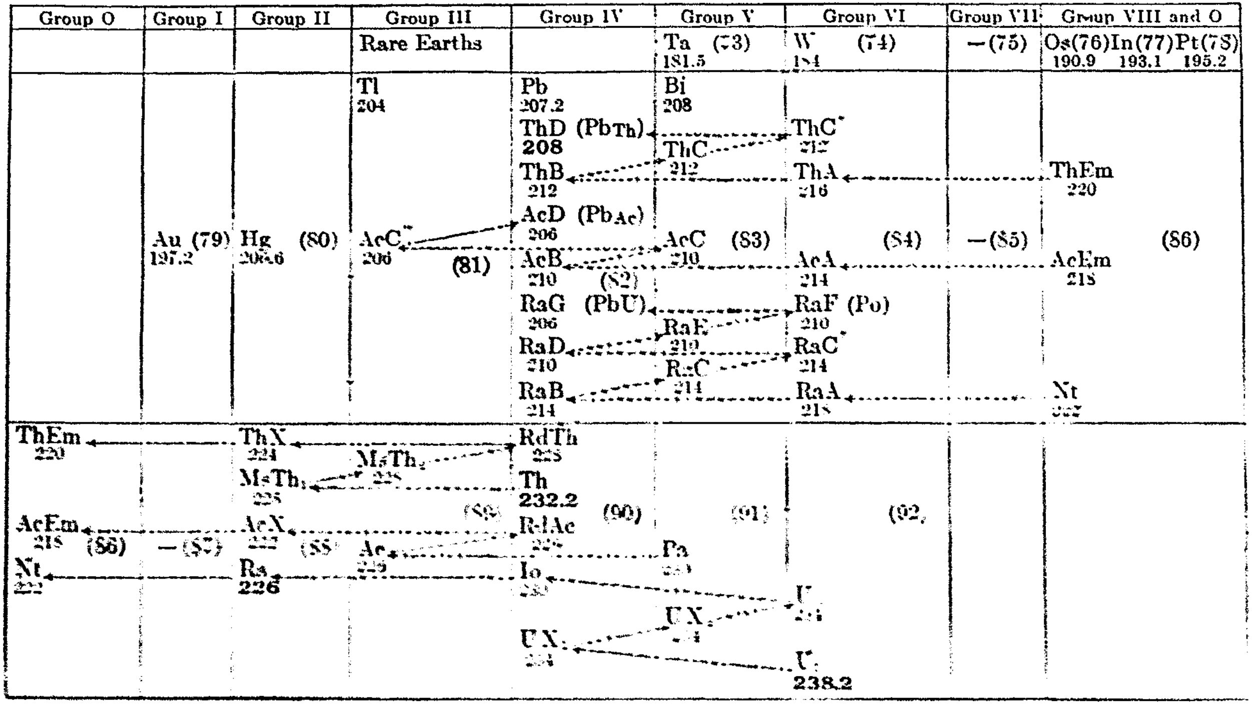
[1] In the actinium series atomic numbers are given because the atomic weights are uncertain.

TABLE XIV



Group O	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII and O
			Rare Earths		Ta (73) 181.5	W (74) 184	—(75)	Os(76)In(77)Pt(78) 190.9 193.1 195.2
			Tl 204	Pb 207.2	Bi 208			
				ThD (PbTh) 208	ThC 212	ThC' 212		
				ThB 212		ThA 216		ThEm 220
	Au (79) 197.2	Hg (80) 200.6	AcC'' 206 (81)	AcD (PbAc) 206	AcC (83) 210	(84)	—(85)	(86)
				AcB 210 (82)		AcA 214		AcEm 218
				RaG (PbU) 206	RaE 210	RaF (Po) 210		
				RaD 210	RaC 214	RaC' 214		
				RaB 214		RaA 218		Nt 222
ThEm 220		ThX 224	MsTh_2 228	RdTh 228				
		MsTh_1 228	(89)	Th 232.2 (90)	(91)	(92)		
AcEm 218 (86)	—(87)	AcX 222 (88)	Ac 226	RdAc 226	Pa 230			
Nt 222		Ra 226		Io 230		U_{II} 234		
					UX_2 234			
				UX_1 234		U_{I} 238.2		

It is to be noted that the branch series usually represents only a very small proportion of the atoms and that these quickly revert to stable atoms. In the case of *U* it is possible that the branch series may give rise to the actinium series, but this is not yet definitely established.

The final product of each series is an isotope of lead. But according to the theory lead from radioactive sources should be exactly like ordinary lead except that it should differ from it in mass. A remarkable confirmation of the theory comes from the fact that lead from radioactive minerals has been found[1] to have a different atomic weight from that shown by ordinary lead. The values check remarkably well with those required by the theories.

Another confirmation of the theories of radioactivity comes from the discovery[2] of the element protoactinium. Actinium was for a time considered the primary radio-element of its series, but it was recognized that it might be the decomposition product of an unknown parent. If such a parent substance exists it must produce actinium by the loss of either a beta particle or an alpha particle. If the former takes place, then the parent would have an atomic number 88, atomic weight 226, and must fall in Group II and be an isotope of radium. Such a substance would be indistinguishable from radium itself. If, on the other hand, actinium is formed from its parent by the loss of an alpha particle, then the mother substance should have an atomic number 91 and should bear the same relationship to tantalum that radium bears to barium. Hence tantalum salts might be used to concentrate the element. When soluble tantalum salts were first added to pitchblende residues, then extracted and purified, it was found that they had become radioactive and that the radioactive element extracted in this way yielded actinium on disintegration. The new element has been named protoactinium (or protactinium), Pa, atomic weight 230 and atomic number 91. It, in turn, may be the disintegration product of uranium. (See Tables XIII and XIV.)

As soon as the fact was established that radium disintegrates,

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[1] Soddy and Hyman, *Proc. Chem. Soc.* **30** 134 (1914); T. W. Richards and his co-workers, *Jour. Am. Chem. Soc.* **36** 1329 (1914); **38** 221, 1658, 2613 (1916); **39** 531 (1917); **40** 1403 (1918); **42** 1550 (1920); Summary, *Smithsonian Report*, 1918, p. 205.

[2] Hahn and Meitner, *Physik Zeit.* **19** 208 (1918) and **20** 127 (1919).

yielding niton and helium, the question arose: "Shall radium be considered as an element or as a compound of niton and helium?" The general belief now is that radium is to be considered an element and that its disintegration is a phenomenon entirely different from chemical decomposition. The reasons for this belief are as follows: —

(1) Radium has a spectrum which resembles that of an element rather than that of a compound.

(2) While the radium atoms are intact they obey the same laws as other atoms, such as the laws of definite and multiple proportion.

(3) The rate of disintegration is independent of all physical conditions. (See pages 65–67.)

(4) The disintegration of radium is accompanied by the emission of particles, a fact which is not duplicated in a single purely chemical reaction.

(5) The evolution of heat during the disintegration of radium is vastly greater than during any known chemical change.

(6) The disintegration of the radium atom is independent of the chemical combination in which it is placed, and proceeds at the same rate whether the atom is in the metallic state or in combination as a halide, carbonate, sulfate, etc.

Consequently, the decay of radioactive atoms is considered a phenomenon which is produced by forces within the atom itself, and is quite a different type of behavior from the disruption of a molecule of a compound.

If the theory of the degradation of radioactive elements is correct, then radium is a product of the disintegation of uranium, and the former should always be present in ores of the latter. This is found to be the case. Moreover since uranium yields radium and radium in turn disintegrates giving other radioactive elements, a balance[1] must be established and there should be a definite ratio between the amounts of uranium and radium in their ores. The ratio between the two elements in various samples of pitchblende has been shown to be constant,[2] but for a considerable time it was supposed that the ratio in

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[1] It must be observed that this is not an equilibrium in the usual sense, since the reactions involved are not reversible.

[2] See Boltwood, *Am. Jour. Sci.* **18** (iv) 97 (1904); Gleditsch, *Le Radium*, **8** 256 (1911); Pirret and Soddy, *Phil. Mag.* **21** (vi) 652 (1911); Marckwald and Russell, *Ber.* **44** 777 (1911).

carnotite was not the same as that in pitchblende. But a careful study[1] of the radium-uranium ratio in carnotite ores has shown that the ratio is 3.33×10^{-7}, which is identical with that found in pitchblende. This is a splendid confirmation of the truth of the theory.

A study of Tables XIII and XIV makes clear the significance of the terms isotope (meaning the same place) and isobar (meaning the same weight). Isotopes are elements occupying the same position in the periodic table with the same chemical and physical properties except mass as, for example, Thorium (232) and Ionium (230), both with atomic number 90. Isobars are elements occupying different positions in the periodic table, having different valences and different chemical properties, but the same atomic weights, *e.g.* Thorium B (212) in Group IV, resembling lead, and Thorium C (212) in Group V, isotope of bismuth. It is evident that the change of an element into its isotope involves a change in atomic weight, whereas the transmutation of an element into its isobar involves a change in properties. The latter is produced by the loss of a beta particle, a negative electron, from each atom. Is this transformation unique among radioactive elements or do we have analogies among the common elements?

To answer this question consider[2] the relationship between ferrous and ferric iron. These two forms of iron have the same atomic weight and they differ in valence, chemical properties (one resembling magnesium and the other aluminium), and in absorption spectra. We may change a ferrous salt to a ferric by the removal of a negative charge or electron. So ferrous and ferric iron appear to be isobars. But there is one very essential difference to be kept in mind. The change of ferrous to ferric is easily reversible and wholly within laboratory control, while the change of a radioactive element into its isobar is spontaneous and so far as we know now quite irreversible. It seems quite reasonable to assume that in one case the radiated electron comes from the outer ring of the atomic structure, and in the other case it comes from the nucleus of the atom.

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[1] Lind and Whittemore, *Bur. of Mines Technic. Paper* 88 (1915).

[2] See Stewart, *Recent Advances in Inorganic Chemistry.*

RADIUM

Uses. — Radium compounds find a limited use in such instruments as the spinthariscope, Fig. 6, and Strutt's radium clock. The latter is an electroscope so arranged that the leaves are alternately charged by radium and discharged by grounding. It is a curious contrivance which transforms the radiating energy of radium into motion which approaches perpetual. (See Fig. 7.)

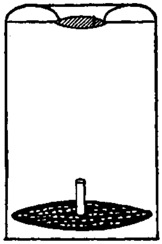

FIG. 6. — SPINTHARISCOPE

The two most important commercial uses for radium compounds at present are in medicine and in the manufacture of luminous paint.

The use of radium in medicine depends upon its ability to check the growth of animal cells. It has been found to be efficient in the cure of surface cancer, warts, lupus, and ulcers. The penetrating gamma rays check the progress of such undesirable growths. Radium has recently been used for the bloodless "removal" of tonsils. It is also claimed that the emanation of radium (niton) relieves gout, rheumatism, and diabetes, because it increases the excretion of uric acid. It is administered either by inhalation or by drinking its solution.

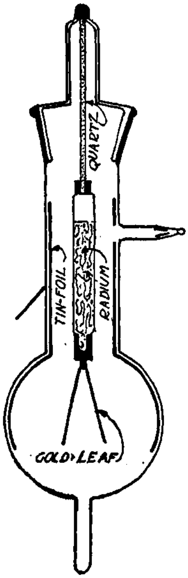

FIG. 7. — RADIUM CLOCK

Many conflicting statements are made by medical men concerning the efficiency and safety of radium treatment for cancer. It is probable that many of the failures have resulted from the use of too little radium or from lack of skill in its use. It seems certain that radium treatment has been wonderfully successful in curing certain types of cancer. Its use for this purpose is increasing rapidly. On account of the high cost of the material other sources of gamma radiation have been used, such as mesothorium, radiothorium, and radium emanation. Since the latter is the most concentrated, it is the most effective. Although the emanation deteriorates rapidly, on account of the intensity of its action and relative low cost it is being used with increasing frequency. So important do medical men consider this use of radium material that they have demanded legislation forbidding the use of radium for luminous paints.

The use of radium in self-luminous paints depends on the fact that when the alpha particles with their appreciable momentum strike some specially prepared zinc sulfide crystals a glow is produced. The material is prepared by mixing a radium salt, usually the neutral chloride or bromide solution, with the phosphorescent zinc sulfide and drying in the dark. Then a paste is made with varnish and some solvent like amyl alcohol, care being taken not to destroy the crystalline structure of the zinc sulfide. The mixture is applied with a brush, after which it is dried and a protective coating of white shellac added. The latter lengthens the life of the paint but lowers its luminosity, probably by interfering with the alpha radiation. The amount of radium used is exceedingly small. The British Admiralty specified for its war-time use 0.4 milligram of $RaBr_2$ per gram of ZnS. In the United States a smaller proportion of radium is used, generally from 0.1 to 0.25 milligram of the element per gram of ZnS. Where low luminosity and long life are desired, as little as 0.01 milligram of radium is used for a gram of ZnS. The statement is made that a luminous watch dial contains from 10 to 20 cents' worth of radium.

The degree of brightness of such luminous surfaces has been determined as of the order of 10 microcandles per square centimeter. This may be compared roughly to the brilliancy of a piece of white paper illuminated by the light of the full moon. When the paint is first prepared, its brightness increases rather rapidly for 10–20 days, then it diminishes gradually for a much longer period, after which the luminosity remains almost constant for several years. The final exhaustion of the paint may be caused either by the failure of the radioactive principle or of the zinc sulfide. The radium seems to be able to produce luminosity for a long period of years, so the zinc sulfide crystals are exhausted first and become incapable of responding to the alpha bombardment. This exhaustion occurs more rapidly when the per cent of radium is larger. Thus the luminous paint prepared under the specifications of the British Admiralty loses half its brilliancy in a year, while the American paints, which are less luminous at first, do not deterioriate to half value in less than 4 or 5 years.

The luminous paint industry received a tremendous stimulation during the war. Not only was the luminous watch dial a great convenience, but instruments which could be quickly and accurately read at night became an absolute necessity in the navy, in the air service, and wherever an ordinary light could not be used. It is said that a single airplane, equipped for night flying, required nine different instruments with luminous dials. One American firm claims to have sensitized over a half million dials for the United States Government. The consumption of radium for this purpose was at one time as much as 500 milligrams per month.

After the war-time demand had ceased, other applications of the paint were made and quickly became popular. Now, in addition to watch and clock dials, luminous paint is used to mark street signs, door plates, push buttons, or almost anything that may need to be located in the dark. The amount of radium used in this manner has been enough to cause serious concern in regard to the future supply, but the largest use of radium at present is in treating cancer.

Attempts are being made to improve the color of precious stones by radium treatment; in some cases the treatment has been successful, but in other cases injury has resulted.

Compounds. — Not many of the compounds of radium have been studied carefully, owing to the scarcity of the material. They resemble quite closely the analogous barium compounds. Their peculiar nature is shown by the fact that they are always somewhat warmer than their surroundings, due to the considerable heat which they are continually radiating. Radium salts produce a carmine color in the flame. The principal salts are as follows: —

Radium chloride, $RaCl_2$ or $RaCl_2 \cdot 2H_2O$, forms colorless crystals when pure; but when barium is present the color is yellow or pink. It is somewhat less soluble in water and hydrochloric acid than is $BaCl_2$, with which it is isomorphous.

Radium bromide, $RaBr_2$ or $RaBr_2 \cdot 2H_2O$, is the salt most commonly used in purifying radium material. It gives off bromine in the air, forming the hydroxide.

Radium hydroxide, $Ra(OH)_2$, is also used in purifying radium. It is strongly basic, absorbing carbon dioxide from the air.

Radium carbonate, $RaCO_3$, is insoluble like the alkaline earth carbonates and is precipitated by adding $(NH_4)_2CO_3$ to the solution of a radium salt.

Radium sulfate, $RaSO_4$, is less soluble than $BaSO_4$, the two being commonly precipitated together.

Radium nitrate, $Ra(NO_3)_2$, is soluble and is formed by dissolving the carbonate in HNO_3.

Detection and Estimation. — The detection of radium may be made by its effect upon the photographic plate. In testing ores the length of exposure necessary to obtain a given result may be used in a roughly quantitative fashion. The discharge of the spectroscope is a sensitive test for radium and may be used quantitatively by observing the time and distance at which discharge is produced. The radioscope, Fig. 8, is an instrument arranged to detect radium emanation by its effect upon phosphorescent zinc sulfide. The emanation is released by previously shaking the finely ground ore with water.

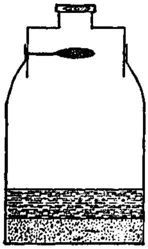

Fig. 8. — Radioscope

The quantitative determination of radium may be made in a number of ways,[1] the method selected being determined by the nature of the material to be analyzed and the degree of accuracy required.

The alpha-ray method consists in comparing the surface radiation of the sample with that of an equal surface of a standard. The method is simple, rapid, and suitable to low-grade material, but is not capable of great accuracy.

The gamma-ray method compares the rate of discharge of the electroscope as shown by the sample and a standard salt. This method is simple and capable of an accuracy of 0.3 per cent. It is best adapted to the analysis of solids comparatively rich in radium, but may be used for material which contains 10^{-10} grams of radium per gram of material.

The emanation method involves the separation of the emanation from the parent radium and measuring the quantity in a special standardized electroscope. The emanation may be removed from solution by boiling or aspiration; the most accurate method of testing a solid is to inclose it in a container for a month or more and test the emanation which is in equilibrium with the radium present.

Radium may also be determined by precipitation as the sulfate.

In speaking of the strength of any radioactive body it is customary to speak of the grams or milligrams of radium which are equivalent. Thus

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[1] See S. C. Lind, *Jour. Ind. and Eng. Chem.* **7** 406, 1024 (1915); **12** 469 (1920); V. F. Hess, *Proc. Am. Electrochem. Soc.* Baltimore meeting (1922); Hess and Damon, *Phys. Rev.* **20** 59 (1922); Owen and Page, *Proc. Roy. Soc.* **34** 27 (1921); B. Szilard, *Compt. rend.* **174** 1695 (1922); N. E. Dorsey, *Jour. Opt. Soc. Am.* **6** 633 (1922).

the expression "one milligram of mesothorium" does not mean a milligram of weight of the element mesothorium but such a quantity of this element as would give a gamma ray activity equal to that of a milligram of radium in some compound such as radium chloride.

A unit sometimes used is the *curie*. It is the amount of radium emanation in equilibrium with a gram of radium metal. So a curie expels the same number of alpha particles per second as a gram of radium.

Likewise the intensity of every product of the uranium-radium series should be expressed in terms of the radium equivalent. Thus "ten milligrams of polonium" signifies an amount of polonium which would be in equilibrium with ten milligrams of radium element or ten millicuries of emanation.

MESOTHORIUM[1]

The heavy demand for radium and its scarcity have greatly stimulated search for a suitable substitute. Ionium would be ideal if it could be obtained pure, but the most successful substitute for radium is mesothorium.

This element was first identified and described by Otto Hahn in 1905. It is the first decomposition product of thorium (see Tables XIII and XIV) and in reality is composed of mesothorium 1, an isotope of radium, and mesothorium 2, an isotope of actinium and analogous to lanthanum in properties. Hahn regarded the former as rayless, with a half-life period of 5.5 years, and the latter as emitting both beta and gamma radiations with a half period of 6.2 hours. The decay of mesothorium 2 produces radiothorium, an isotope of thorium, with a half period of two years, yielding alpha radiations. Consequently, after mesothorium has stood for a time it consists of an equilibrium mixture of mesothorium 1, mesothorium 2, and radiothorium, from which alpha, beta, and gamma radiations are expelled. It is to be noted that radiothorium, which is always present in thorium minerals, cannot be separated from thorium by any known method. The only source of radiothorium is mesothorium.

Mesothorium is more active than radium. From a study of the half-life ratio between mesothorium and radium (6 : 1800), Hahn concluded that a milligram of mesothorium by weight should be as active as 300 milligrams of radium. The U. S.

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[1] See Otto Hahn, *Zeit. anorg. Chem.* **24** 1110; *Chem. Ztg.* **35** 845 (1912); *Bur. of Mines Technical Paper* No. 110, and especially *Bur. of Mines Technical Paper* No. 265 (1922).

Bureau of Mines says that mesothorium is three times as active as radium, weight for weight.

Mesothorium is found in all thorium minerals. The ratio between the two elements as determined by McCoy[1] is 0.52×10^{-7}. The reciprocal of this ratio $19. \times 10^6$ is the weight in grams of thorium in equilibrium with a quantity of mesothorium which has a gamma ray activity equivalent to one gram of radium. Hence, a metric ton of monazite sand containing 5 per cent ThO_2, which is subjected to 90 per cent extraction, would yield 2.5 milligrams of mesothorium. The importation of monazite into the United States in 1914 was 385 metric tons, from which a little less than a gram of mesothorium could be extracted. The world's consumption of monazite at present is estimated as about 3000 tons annually. On the same basis this would yield between 6.5 and 7.0 grams of mesothorium. This would be almost a forlorn hope as a source of material to be used as radium substitute, were it not for the fact that the mesothorium is a by-product and that very large quantities of monazite residues have been stored up. Previous to the entry of the United States into the war there had been no mesothorium extracted in this country. But because of the enormous war demand for luminous paints, methods were devised for extracting this material. The principle involved in the separation is based upon the fact that mesothorium is like radium chemically. Consequently, the separation of mesothorium-barium precipitates is similar to the separation of radium-barium which has already been outlined. Mesothorium is said to be extracted from monazite now used in the United States.

Since monazite contains an appreciable amount of uranium, radium is always present and the methods of extracting mesothorium concentrate the radium also. Consequently, commercial mesothorium contains considerable radium, which is responsible for 20–25 per cent of the radioactivity produced. Since, however, the mesothorium is much more active than radium, it is estimated that commercial mesothorium is composed, weight for weight, of 99 per cent radium chloride and 1 per cent mesothorium chloride.

When first extracted, mesothorium is useless for the manufacture of luminous paint, but as the amount of radiothorium

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[1] McCoy and Henderson, *Jour. Am. Chem. Soc.* **40** 1316 (1918).

increases the alpha radiation increases, making it more efficient in luminous paints. The maximum alpha radiation is reached after four or five years. Consequently, it is customary to allow freshly prepared mesothorium to "ripen" for a year or more in order to develop its alpha radiations. After reaching its maximum, mesothorium decays at a much faster rate than radium, losing one-half its luminosity every five or six years.

During the ripening process mesothorium is emitting beta and gamma radiations and is serviceable in medicine for the same purposes as radium. It has not become popular with the medical profession, probably because its relatively short life makes its final cost high.

Mesothorium is not a common article of commerce, so can scarcely be said to have established a market price. In 1913, it sold in England for £5 per milligram equivalent. In the United States it has sold as high as $75 per milligram equivalent, but the usual price runs from 40 to 60 per cent of that of radium for an equivalent gamma radiation. In 1921 the price ranged around $60 for an amount equivalent in activity to one gram of radium element.

The development of mesothorium in medicine does not look encouraging as long as the supply of radium is sufficient to meet the demand. But its use in luminous paint seems to have been well developed in Europe. It is particularly well adapted for this purpose, especially for objects which are themselves rather short-lived, and it is to be hoped that its use will increase in order to conserve the radium supplies for medical purposes.

The separation and estimation of mesothorium are accomplished by the same methods that are used for radium.[1]

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[1] See *Bur. of Mines Technical Paper* No. 110, pp. 25–27.

CHAPTER V

GROUP II — BERYLLIUM

THE first four members of Division B show a striking family resemblance, with gradual changes in properties. Mercury in many respects resembles copper, as for example in the numerous ammoniacal compounds formed. Zinc, cadmium, and mercury form a typical triad; beryllium and magnesium resemble each other closely and form a connecting link between the alkaline earths and the zinc sub-group. The vapors of all five metals of this division are composed of monatomic molecules. The physical properties are shown in Table XV.

TABLE XV

Constants of the Magnesium Family

	BERYLLIUM	MAGNESIUM	ZINC	CADMIUM	MERCURY
Atomic Weight	9.1 [1]	24.32	65.37	112.4	200.6
Specific Gravity	1.64	1.75	7.1	8.6	13.6
Melting Point	1280°	633°	419°.4	321°	–38°.7
Boiling Point		1120°	918°	778°	357°
Atomic Volume	5.5	13.8	913	13	15.4

The members of Division B differ from the alkaline earth metals by being more easily reduced to the metallic state; all the elements are stable in the air at ordinary temperatures, except beryllium, which is slowly oxidized in moist air; the ease of reaction with steam decreases with increased atomic weight.

The compounds of these elements are all bivalent, except in the mercurous series, and resemble the corresponding compounds of the alkaline earths except that they show a greater tendency to form basic compounds. Division B sulfates are

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[1] Hönigschmid and Birckenbach, *Ber.* **55B** 4 (1922) obtained the value 9.018 from a study of the ratios beryllium chloride to silver chloride and to silver.

soluble and crystalline, readily forming double sulfates, with the exception of $HgSO_4$. The hydroxides are nearly insoluble and are more easily decomposed by heat than the hydroxides of Division A.

Historical. — In 1797, Haüy, a mineralogist, found that the minerals beryl and emerald had the same physical structure, hardness, and specific gravity. He asked Vauquelin to make a chemical analysis to see if they were not of the same composition. In the course of the analysis Vauquelin found that while these two minerals were of the same composition they both contained an oxide very similar to alumina but differing from it in the fact that it was precipitated from its KOH solution by boiling. Further study showed other peculiarities; its salts had a sweet taste; its hydroxide was soluble in dilute ammonium carbonate; and its sulfate formed irregular crystals but no alum with K_2SO_4.

In his published account Vauquelin unfortunately failed to give the new element a name, but referred to it as "the earth of beryl." The editors of the *Annales de Chimie* suggested the name glucina, meaning sweet, because of the peculiar taste of its salts. This name, however, was not universally accepted, especially when it was recalled that a sweet taste is not peculiar to the compounds of this element. The German chemists used the name "beryl earth," from which the name beryllium was applied to the element. Whether the element shall be called glucinum or beryllium seems to depend rather upon personal preference than upon any other consideration.

The preparation of metallic beryllium has been attended with some difficulties. Sir Humphry Davy attempted to reduce BeO with potassium vapor but failed. Later he fused iron filings and BeO, obtaining[1] a metallic mass, somewhat malleable, which was probably an alloy of iron and beryllium. Wöhler, in 1827, prepared metallic beryllium for the first time, reducing $BeCl_2$ with potassium and removing the KCl from the impure beryllium by the greater solubility of the former.[2]

Occurrence. — Beryllium occurs in a large number of minerals, some of which are quite common and contain a considerable amount of the element. Beryl, $Be_3Al_2(SiO_3)_6$, contains roughly 14 per cent BeO; chrysoberyl, $BeO \cdot Al_2O_3$, contains 19.8 per cent BeO; phenacite, $2\,BeO \cdot SiO_2$, contains 45 per cent BeO; and gadolinite,[3] $Be_2Fe(YO)_2(SiO_4)_2$, contains about 10 per cent BeO. In addition beryllium is found in many less familiar minerals, in some of which BeO makes up more than half the weight of the material.

The best known and most important mineral is beryl, which

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[1] *Phil. Mag.* **32** 152 (1808).

[2] Pogg. *Ann. der Physik und Chemie*, **13** 577 (1828).

[3] *Jour. Am. Chem. Soc.* **38** 875 (1916).

is known in a variety of forms. In the common opaque form, beryl is found in large hexagonal prisms sometimes weighing as much as a ton each. In the transparent forms, which are much more rare, the color may be green, blue-green (aquamarine), yellow (golden beryl), blue, or red (rose beryl). Emerald is a variety of beryl which owes its bright green color to chromium. The common beryl is widely distributed over the United States, deposits being reported in nearly all the New England states, in Virginia, Pennsylvania, Alabama, Colorado, and other states. Numerous deposits are reported from France, especially in the Vosges, where an exaggerated saying states that the streets of Limoges are paved with emeralds. Particularly rich and extensive deposits are found in Madagascar.

It has been estimated that beryllium comprises between 0.01 and 0.001 per cent[1] of the earth's crust, and there is reason for the common belief that when the commercial uses for beryllium become considerable enough beryl will be found to supply any possible demand.[2]

No reliable information is obtainable in regard to the recent production of beryl in the United States. It is estimated that during 1919 the total production did not exceed 25 tons of ore. The usual product contains 10–12 per cent BeO and sells at 3–4 cents per pound wholesale at the mines.

Extraction. — A very large number of methods have been proposed for the decomposition of beryl,[3] which is considered the only commercial source of beryllium.

Gibson's method[4] is based on the principle that ammonium hydrogen fluoride effects the complete decomposition of beryl at a low temperature, even if the mineral is only coarsely ground. Much of the silica is volatilized as ammonium fluosilicate and the beryllium and aluminium converted first to fluorides, then sulfates. The former is separated by solution in $(NH_4)_2CO_3$.

Lebeau's method[5] fuses the ground mineral with CaF_2,

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[1] J. H. L. Vogt, *Trans. Am. Inst. M. E.* **31** 128 (1902).

[2] H. Copaux, *Chimie et Industrie*, **2** Aug. (1919) and J. S. Negru, *Chem. and Met. Eng.* **21** 353 (1919).

[3] See Parsons, *Chemistry and Literature of Beryllium*, 1908, Chem. Pub. Co., Easton, Pa.; Copaux, *Compt. rend.* **168** 610 (1919); Negru, *Chem. and Met. Eng.* **21** 353 (1919); also, James and Perley, *Jour. Amer. Chem. Soc.* **38** 875 (1916).

[4] *Jour. Chem. Soc.* **63** 909 (1893).

[5] *Compt. rend.* **121** 601 (1895).

and adds H_2SO_4 to the melt. Silica is expelled as SiF_4, while the aluminium and beryllium appear as sulfates. The excess acid is neutralized by K_2CO_3 and on evaporation most of the alumina separates as $KAl(SO_4)_2 \cdot 12\,H_2O$. Ammonium carbonate is used to separate the beryllium.

The method proposed by Pollok[1] fuses the beryl with caustic soda, dissolves the mass in HCl, precipitates the hydroxides with NH_4OH, and redissolves in HCl. Then by saturating this solution with HCl gas, the alumina is precipitated as $AlCl_3 \cdot 4\,H_2O$. Finally $(NH_4)_2CO_3$ is used to separate the beryllia.

In Parsons' method[2] the mineral is fused with KOH, dissolved in H_2SO_4 and evaporated to dehydrate the silica. The soluble salts are taken up with water and most of the alumina removed as alum by concentrating the solution. The remainder of the alumina and the iron are removed by a concentrated solution of $NaHCO_3$, while the beryllia is precipitated by diluting and heating the bicarbonate solution.

A method proposed by Copaux[3] disintegrates the ore by heating with sodium fluosilicate at 850°. Silica remains unattacked while beryllium sodium fluoride is formed. This is readily soluble, while the corresponding aluminium salt is nearly insoluble. The small amount of impurities present are removed by converting to the sulfates and crystallizing $BeSO_4 \cdot 4\,H_2O$. This method has been in commercial use in France since 1915.

A study of the efficiency of these methods has been made by I. E. Cooper[4] with the desire to test their efficiency. His conclusions are shown in Table XVI.

These results were obtained on 50-gram samples, and should be considered typical rather than final. They indicate two very serious problems which must be solved before the large-scale extraction of beryllia can become a considerable commercial success: (1) obtaining BeO fairly free from impurities, especially iron and aluminium; (2) devising a method by which better yields can be obtained. The necessity for efficient methods is evident from the lightness of beryllium itself. Thus

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[1] *Trans. Roy. Dublin Soc.* **8** 139 (1904).

[2] *Chemistry and Literature of Beryllium.*

[3] *Chimie et Industrie* **2** Aug. (1919).

[4] *Thesis*, University of Illinois, June, 1920.

TABLE XVI

Comparative Methods of Extracting Beryllium

	PER CENT YIELD	PURITY	COST OF CHEMICALS PER G. BeO	REMARKS
Gibson	77.5	impure	$0.11	might succeed on large scale
Lebeau	50.	very impure	0.16	long and troublesome
Pollok	40.	very pure	.19–.22	good
Parsons	20–40.	very pure	.06–.08	process simple but bulky
Copaux	35.	pure	0.26	probably efficient on large scale

a ton of beryl containing 14 per cent BeO would yield a little over 80 pounds of metallic beryllium if both the extraction and reduction were 90 per cent efficient.

Separation. — Beryllium is precipitated from its solutions by alkalies along with aluminium and iron, with which it is commonly associated in nature. $Be(OH)_2$ resembles $Al(OH)_3$ in being soluble in excess of fixed alkali, but differs[1] from it in that $Be(OH)_2$ is reprecipitated on boiling while $Al(OH)_3$ is not. One of the most satisfactory methods of separating aluminium from beryllium is by boiling a solution to which just enough 6 N NaOH has been added to dissolve the precipitate which first forms. A saturated solution of sodium acid carbonate dissolves $Be(OH)_2$ but not $Al(OH)_3$ or $Fe(OH)_3$. If a mixture of $AlCl_3$ and $BeCl_2$ is taken up with water and ether, and HCl gas added, $AlCl_3 \cdot 4\,H_2O$ is precipitated, while the beryllium remains in solution. By adding hot glacial acetic acid to a mixture of acetates, basic beryllium acetate separates on cooling. Fusion with Na_2CO_3 converts Al_2O_3 into soluble $NaAlO_2$, while BeO remains insoluble; fusion with Na_2SiF_6 produces soluble Na_2BeF_4 and insoluble Na_3AlF_6.

In each of these methods conditions must be very carefully

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[1] See H. T. S. Britton, *Analyst*, 46 359 and 437 (1921); 47 50 (1922).

regulated, since the behavior of beryllium is very markedly influenced by minor conditions. These relations are not well understood at present, hence the separation of beryllium presents unusual difficulties.

Metallurgy. — The fused beryllium halides are almost nonconductors of the electric current, consequently, the metal cannot be prepared by the electrolysis of the fused simple halides. If $BeCl_2$ is mixed with NaCl and NH_4Cl, or BeF_2 with NaF, the electrolysis may be carried out successfully. The removal of the metal from the electrolyte presents some difficulties. The melting point of the metal is higher than that of the bath, consequently the beryllium separates in flakes, which must be separated from the mixed fluorides. This separation is laborious because the fluorides are difficultly soluble in water and if the water becomes either alkaline or acid the metal itself will dissolve. Secured in this manner the metal is in the form of small flakes which may be melted and run into ingots by heating in a vessel of magnesia or beryllia in a stream of hydrogen. Beryllium oxide dissolves readily in fused cryolite and the solution on electrolysis yields beryllium or its alloys; electrolysis of a mixture of barium fluoride and sodium beryllium fluoride is also a promising method of obtaining the metal and its alloys.[1]

Beryllium has also been prepared[2] by other methods: (1) Beryllium chloride is easily reduced by sodium or potassium, but the chloride must be in the anhydrous condition and its preparation is very troublesome. (2) The Goldschmidt process yields metallic beryllium containing about 10 per cent aluminium. The application of external heat is necessary in order to raise the temperature above the melting point of beryllium. (3) Potassium beryllium fluoride mixed with sodium and heated strongly gives metallic beryllium.

Metallic beryllium has never been obtained except in small quantities. The metal is quoted (1913) at $3.75 per quarter gram, which is about four times the war price for platinum. This value is entirely artificial, and when beryllium ores are successfully reduced the metal will be both reasonable in price and plentiful in amount. It may never, however, become a

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[1] See E. A. Engle's *Thesis*, University of Illinois.

[2] See *Jour. Am. Chem. Soc.* **38** 875 (1916).

common metal on account of the small amount obtainable from its ores.

Properties. — Many conflicting statements are made in regard to the properties of beryllium, doubtless because of the difficulty of obtaining the element in pure form. Small amounts of impurities would be expected to influence its properties greatly.

Beryllium is described[1] as silvery white (or steel gray) in color, with a hardness of 6 or 7 on Moh's scale. It is malleable, easily forged and cold rolled, takes a high polish, but its tensile strength and rigidity are not known. Its specific gravity is 1.64 (older values run as high as 1.8); its specific heat is probably the highest of any of the useful metals, varying with temperature up to 400°–500°, where it becomes constant at 0.62; the latent heat of fusion is very high, in the neighborhood of 300 calories; the latent heat of vaporization is probably the highest of all elements except carbon and boron; its electrical conductivity[2] is higher than that of copper, approaching silver in this respect. Positive ray analysis[3] gives no indication of the presence of isotopes.

The metal is more permanent in the air than magnesium, oxidizing slowly and superficially in moist air. When heated to redness in oxygen it oxidizes on the surface, the oxide so formed acting as a protective coating. When the powdered metal is heated in the air it burns brilliantly, forming the oxide. The heat of oxidation was determined indirectly by Copaux and Phillips[4] and found to be 151.5 Cal. This places beryllium immediately after calcium and just before lanthanum in the table of heats of oxidation of the elements. Water or steam is not decomposed even at red heat. When heated in the electric arc in an atmosphere of hydrogen it sublimes, forming a gray mirror which resembles arsenic. It does not unite directly with sulfur vapor but combines with chlorine and bromine, producing an incandescence. The reaction with iodine is more difficult. At the temperature of the electric

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[1] See especially *Chem. and Met. Eng.* **21** 353 (1919).

[2] See *Chem. and Met. Eng.* **21** 353 (1919); H. Copaux in *Chimie et Industrie*, **2** 914 (1919), claims that the electrical conductivity of beryllium is one quarter that of magnesium and one seventh that of aluminium.

[3] G. P. Thomson, *Nature*, **107** 395 (1921).

[4] *Compt. rend.* **171** 630 (1920).

furnace it unites with silicon, forming a hard, brittle mass which takes a high polish. It unites directly with both carbon and boron and alloys readily with many metals. HCl gas attacks it at slightly elevated temperatures and the solution dissolves it easily, liberating hydrogen. It reacts with concentrated H_2SO_4, liberating SO_2, and with the dilute acid, yielding hydrogen. HNO_3 has very slight action on it even at the boiling temperature. It is not attacked by ammonia, but dissolves easily in KOH solution, liberating hydrogen.

Uses. — The most promising use of metallic beryllium is in connection with the formation of alloys, many of which have been studied briefly. Of these the aluminium alloy has attracted particular attention because of the lightness of both metals and the hardness and strength of the alloy. These metals alloy in all proportions. The mixture of 90 per cent aluminium and 10 per cent beryllium [1] has a specific gravity of 2.5. The addition of beryllium to the alloys of calcium and aluminium increases the solubility of calcium in aluminium and makes a tougher and more malleable product. An alloy of 85 per cent aluminium, 10 per cent beryllium, and 5 per cent copper has a specific gravity of 2.8 with a tensile strength and toughness equal to bronze.

An alloy with a specific gravity as low as 1.5 may be made by using up to 25 per cent lithium with beryllium. This product oxidizes superficially, after which it is said to be as resistant to corrosion as iron. Alloys of beryllium with magnesium are impossible [2] to make by direct methods, because the latter boils at a temperature below the melting point of the former.

The alloys of beryllium and copper have received much study. These alloys are of value in making scientific instruments on account of their electrical properties. They also possess a resonance of excellent quality and are prized for the making of musical instruments.

Beryllium and silver alloy readily, forming a eutectic at 878° with 16 atomic per cent of beryllium. These alloys increase in hardness and diminish in ductility as the per cent of beryllium increases.

Alloys of iron containing up to 21 per cent beryllium have been made, a eutectic being formed at 1155° with 38.4 atomic

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[1] *U. S. P.* 1, 333, 965, March 16, 1920.

[2] *Zeit. anorg. Chem.* **97**, 6 (1916).

per cent of beryllium. Alloys with chromium, molybdenum, tungsten, and other metals have been prepared.

A suggested use for beryllium which possesses unusual possibilities is as a cleansing agent in the manufacture of aluminium.

Beryllium oxide finds an important use in connection with the manufacture of incandescent gas mantles. From two to five grams of beryllium nitrate are added to a kilogram of the lighting fluid. The small amount of BeO thus added to the mantle gives greater strength, and is particularly serviceable for mantles which are given special shapes, such as those for use with a pressure system. Beryllium nitrate is sometimes added to the collodion used for mantle coating to increase the protection given to the mantle.

Some possible uses of beryllium oxide are also suggested in the following fields: (1) Esters have been successfully prepared by passing the vapors of the acids and alcohols over moderately heated beryllium oxide. This is especially successful in the case of aliphatic acids where a temperature little above 300° is required. (2) Another interesting possibility is the use of BeO as a refractory for crucibles. It melts at 2450°, which classes it with zirconia and magnesia. Its density (*d* = 3) is a little lower than magnesia (3.22) and it is a much weaker base than magnesia and resists acid corrosion much more effectively after calcination. (3) BeO has also shown some promise in the preparation of abrasives, synthetic gems, dental products, and paint bases.

Beryllium salts find a limited use in pharmaceutical preparations. They are also used in organic syntheses.

Compounds. Beryllium is bivalent only. It does not form peroxides like the alkali metals nor subchlorides like the alkaline earths. Its compounds resemble those of aluminum most closely.

BeO is a white amorphous powder best obtained by ignition of the basic carbonates; it is insoluble in water and unchanged by it. It is easily soluble in dilute acids if it has not been strongly ignited. When fused in an electric arc it forms a crystalline mass which is harder than rubies; it is soluble in hot concentrated acids only. It is basic, but also feebly acidic.

$Be(OH)_2$, white gelatinous, is precipitated from beryllium solutions by NH_4OH. It is soluble in acids, in fixed alkalies, and in alkaline carbonates. On drying it becomes less soluble and on ignition it yields BeO.

With the halogens, beryllium forms the simple salts BeX_2 which are easily hydrolyzed, the chloride, bromide, and iodide being almost completely hydrolyzed; the iodide is difficult to form and reacts readily with organic compounds. The fluoride and chloride form many double salts. The anhydrous chloride is best prepared by passing a current of chlorine over a heated mixture of beryllium oxide and carbon or over the hot carbide.

$Be(NO_3)_2 \cdot 3\ H_2O$ is extremely hygroscopic and can be crystallized only with difficulty, best from strong nitric acid. When heated on the steam bath it gives a basic salt, $Be \cdot NO_3 \cdot OH \cdot H_2O$, easily soluble in water.

BeC_2 is obtained by heating a mixture of BeO and carbon in an electric furnace. It is slowly decomposed by water and dilute acids, giving pure methane. A basic carbonate of varying composition is precipitated as a fine powder when an alkali carbonate is added to a beryllium solution. When carbon dioxide is passed into a suspension of this basic carbonate the normal $BeCO_3 \cdot 4\ H_2O$ is formed and crystallizes with difficulty.

Beryllium sulfate crystallizes with 6, 4, 2, or 1 molecules of water. The anhydrous sulfate is formed at 220° and at red heat BeO is formed. The sulfate forms no mixed crystals with the sulfates of copper, nickel, or iron, as do the other members of the magnesium family.

Beryllium forms double alkali tartrates in which beryllium not only replaces the acid hydrogen but also to some extent the hydrogen of the radical. The presence of the beryllium increases the molecular rotation not only of the tartrates but even more noticeably of the malates.

Basic beryllium acetate is prepared by the action of glacial acetic acid upon the dry carbonate or hydroxide. It is only slightly soluble in water but is hydrolyzed, becoming soluble. It melts, boils, and sublimes without decomposition. It was used by Parsons for his atomic weight determinations.

Detection and Estimation. — Beryllium is detected in qualitative analysis by the reactions which distinguish it from aluminium, zinc, and iron. (See Separation.)

Spectroscopic detection of beryllium has been suggested.[1] Since beryllium salts of themselves give no absorption spectrum, it is necessary to form a lake with some organic coloring matter. Best results are obtained by a dilute alcoholic extract of alcanna root. When the mineral salts are added to this extract, it is possible to detect 1.6 mg. BeO in the presence of 2 grams aluminium and 2.0 mg. BeO in the presence of 2 grams of iron.

For the estimation [2] of beryllium, usually the hydroxide is precipitated by NH_4OH and ignited to BeO.

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[1] H. Brunner, *Dissertation*, Techn. Hochschule in Zurich.

[2] See *Compt. rend.* **168** 612 (1919); also Parsons' *Chemistry and Literature of Beryllium.*

CHAPTER VI

GROUP III THE RARE EARTHS

The elements which comprise Group III include boron as an introductory element and scandium, yttrium, lanthanum, and the rare earth group in Division A, while aluminium, gallium, indium, and thallium are found in Division B. The relationship of the elements is shown in Fig. 9.

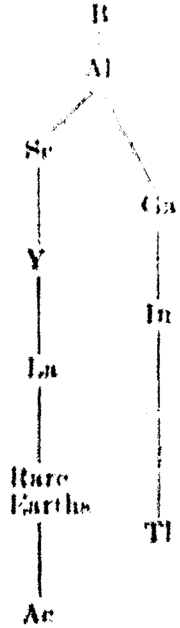

Fig. 9

The relationship of boron is open to question. We should expect it to belong to Division A, while in many characteristics it resembles aluminium. On the other hand, it differs from all other members of Group III by being mainly acidic in nature. Consequently, many authors prefer to treat it separately.

All members of Group III form oxides of the type M_2O_3 and halides MX_3. The basicity of the hydroxides $M(OH)_3$ increases with increase of atomic weight of the metal (except in the rare earth group), the first member of the series, H_3BO_3, being mostly acidic, but acting as a base towards the strongest acids. The oxides of the metals of Division A are more basic than those of Division B. (Compare with Group II.) Accordingly, the hydroxides of Division A are almost insoluble in alkalies, while those of Division B are much more soluble; Division A elements form stable carbonates, $M_2(CO_3)_3$; Division B elements do not; the halides of Division A elements are non-volatile, in general, and but slightly hydrolyzed by water, while the opposite facts are true of the corresponding halides of Division B; all the elements of Group III show a tendency to form double sulfates, but these compounds of Division A elements are not alums. The characteristic valence of all the elements is 3, although thallium forms a well-defined series of univalent salts and several of the rare earth group form peroxides.

The most striking facts concerning this group are in connection with the abundance of the elements. Aluminium is the most abundant metal and the third most abundant element that we know, making up 7.28 per cent[1] of the world which we are able to examine. With the exception of boron all the other elements of this group are scarce, and some of them are among the least common of all the elements of the periodic table.

The Rare Earths

The term "rare earths" is used to designate a group of elements, closely related chemically, which are placed in Division A of Group III. They were called "earths" because their oxides resemble those of the alkaline earths, and the designation "rare" was originally applied because of their scarcity. Now many of these elements are known to exist in considerable quantities, but the term "rare" is still strikingly applicable because of the unique relationships of the group.

The rare earths may be defined as a group of trivalent metals, forming basic oxides, with oxalates insoluble in dilute mineral acids. Their fluorides are also difficultly soluble, hence they may be separated, in general, from other elements by adding oxalic or hydrofluoric acid to their solution, to which some mineral acid has previously been added. Doubtless the most striking fact which characterizes these elements is the remarkable similarity in both the physical and chemical properties of their compounds. Their main differences are in the solubilities of their salts and the basicity of their oxides, which varies between that of the alkaline earths and that of aluminium.

The term "rare earth group" is a rather indefinite one because there are no very sharply drawn boundary lines. Strictly speaking, the term should include only those elements between cerium with an atomic number of 58 and tantalum, 73. This would include the following elements; praseodymium, neodymium, ekaneodymium (undiscovered), samarium, europium, gadolinium, terbium, holmium, dysprosium, erbium,

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[1] Estimate of F. W. Clarke; see his *Geochemistry*.

thulium, ytterbium (neoytterbium), lutecium, and celtium (?). To this should be added the elements scandium, yttrium, and lanthanum, members of Division A and typical rare earths in almost every respect.

Almost invariably cerium is also included, mainly because in its trivalent compounds it is also a typical rare earth. Thorium is likewise generally treated with the rare earth group, because it is found associated with them in nature and resembles cerium closely. It seems more logical, however, to regard thorium as an element which is very closely related to the rare earth group, but not strictly speaking a member of it. Zirconium, columbium, and tantalum are other elements whose positions in the periodic table suggest relationship with the rare earth group. They are commonly found in rare earth minerals and in many respects resemble the rare earth elements. Titanium and beryllium also are somewhat more distantly related to this group of elements.

The position of the rare earth group in the periodic table is, and probably always will be, a puzzling problem. Many chemists follow Mendeléeff in attempting to place its members in successive groups in regular order. This arrangement is not satisfactory because of the difficulty of finding a place for the rare earths and especially because of the fact that the positions give no indication of the properties or peculiar relationships of the individual elements. Probably the most helpful plan for disposing of the rare earths in a flat surface arrangement of the table is to consider the group as occupying the position of a single element in Group III, series 8. A secondary table showing the relationships within the rare earth group is then possible. In the spiral arrangements of the periodic table it is customary to dispose of the rare earth group by continuing the sequence along the surface of the helix parallel to the axis.

Historical. The actual beginning of rare earth history was in 1794 when the Finnish chemist, Johann Gadolin, found a new earth in a mineral which Arrhenius had discovered at Ytterby, Sweden, six years before. In 1797, Ekeberg confirmed this discovery and suggested for the oxide the name yttria from the name of the village, and gadolinite for the name of the mineral. Both Gadolin and Ekeberg considered that the new oxide contained a single metal. The similarity of the members of this group is strikingly shown by the fact that the original yttria was in reality not the oxide of a single metal, but a mixture of oxides of at least 15 or 16 different metals.

The mineral now known as cerite was discovered in 1751, but nothing unusual was observed concerning it until 1803, when Klaproth discovered that it gave an oxide resembling Ekeberg's yttria quite closely. Berzelius and Hisinger made a similar observation simultaneously and the names ceria and cerite were proposed for the oxide and mineral respectively. These names were derived from the planetoid Ceres which was then newly discovered.

It was soon discovered that these oxides were in reality complex, and other oxides were one by one isolated from the original mixtures. The detailed history is long and confusing because of the complex nature of these oxides and the great difficulty in obtaining pure compounds. An outline of the history as it has finally developed is sufficient for the present purpose. See Tables XVII and XVIII.

Table XVII

Historical Development of the Yttrium Group

- Yttria, Gadolin, 1794
  - Erbia — Terbia: Erbia Mosander, 1843 — Terbia Delafontaine, 1878
    - Terbia de Boisbaudran, 1895 Urbain, 1904
    - Gadolinia Marignac, 1886
  - Terbia — Erbia: Terbia Mosander, 1843 — Erbia Berlin, 1860
    - Holmia Cleve, 1879
      - Holmia de Boisbaudran, 1886
      - Dysprosia de Boisbaudran, 1886
    - Thulia Cleve, 1879
    - Ytterbia Marignac, 1878
      - Neo-ytterbia Urbain—Welsbach, 1906–07
      - Lutecia Urbain—Welsbach, 1906–07
      - Celtia (?) Urbain, 1911
    - Scandia Nilson, 1879
  - Yttria Mosander, 1843

According to our best information at the present time the following elements are recognized: scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, holmium, dysprosium, erbium, thulium, ytterbium (or neoytterbium), lutecium, and celtium.[1] There is some evidence for the opinion that "thu

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[1] Coster and Hevesy announce the discovery of hafnium (see *Nature*, Jan. 20, 1923, p. 79), an element of atomic number 72. This element is described as

TABLE XVIII

Historical Development of the Cerium Group

Ceria, Klaproth, Berzelius and Hisinger, 1803	Lanthana, Mosander, 1839	Lanthana, Mosander, 1841		
		Didymia Mosander, 1841	Didymia, de Boisbaudran, 1879	Praseodymia, von Welsbach, 1885 Neodymia
			Samaria, de Boisbaudran, 1879	Europia, Demarçay, 1896–1901 Samaria
	Ceria, Berzelius, 1814			

lium" is a mixture of thulium I, thulium II, and possibly thulium III. The chemical evidence[1] for the existence of celtium is good, but its atomic number has been uncertain. Recent investigations[2] lead to the establishment of the number 70 for ytterbium, 71 for lutecium, and 72 for celtium. Questions have been raised also concerning the individuality of erbium, holmium, dysprosium, terbium, and even cerium, but these are now generally accepted as chemical elements.

The names of the elements of the rare earth group have been derived from a variety of sources. Yttrium, erbium, terbium, and ytterbium are obtained from Ytterby, the Swedish village from which gadolinite was first obtained. Europium, scandium, and celtium are geographical names; holmium was named from Stockholm, lutecium from Lutetia, an ancient name for Paris, and thulium from Thule, an old name for Scandinavia. Samarium obtained its name from samarskite, so called in honor of a Russian mine officer, Samarski, by name; gadolinium was named for Professor Gadolin, and cerium from the asteroid Ceres. Didymium means the twin element, so named because of its close resemblance to lanthanum, from which it was separated; when didymium was found to contain two elements, one was called neodidymium, the new twin, but the name was later shortened to neodymium; praseodymium signifies a green-colored twin. Lanthanum is derived from the Greek verb meaning to lie hidden, and dysprosium signifies difficult of access.

Occurrence. Contrary to the opinion of the discoverers, this group of elements is widely distributed in nature. The minerals are numerous, well scattered, but usually found in small deposits or intimately mixed with other materials. Sili-

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belonging to the zirconium family, which would place it in Group IV between the rare earths and tantalum. If the existence of this element is confirmed, it seems certain that celtium cannot exist as a rare earth element with atomic number 72.

[1] Welsbach, *Monatsch.* **32** 373 (1911); James, *Jour. Am. Chem. Soc.* **33** 1332 (1911).

[2] Urbain, *Compt. rend.* **174** 1347, and Dauvillier, *ibid.* **174** 1349 (1922).

cates are the most common form, phosphates are numerous and important, while halides, carbonates, oxides, titanates, uranates, columbates, tantalates, and zirconates are found in varying degrees of complexity. There are about 150 different rare earth minerals listed.[1] The following are some of the best known: —

Gadolinite, a silicate of beryllium, iron, and yttrium group metals of the typical formula[2] $FeBe_2Y_2Si_2O_{10}$. It usually contains 35–48 per cent yttria, with outside limits of 5–60 per cent. It is found in Norway, Sweden, Texas and Colorado.

Xenotime, a rare earth orthophosphate with ThO_2, SiO_2, ZrO_2, etc. The cerium earths vary from 0 to 11 per cent and yttria from 54.1 to 64.7 per cent. Occurs in the diamond sands of Brazil and in Norway.

Euxenite, $E(CbO_3)_x \cdot E_2(TiO_3)_3 \cdot 1\frac{1}{2}H_2O$ with U, Zr, and Th, contains 2.3 – 8.4 per cent Ce, 13.2 – 34.6 per cent Y, and 20–23 per cent TiO_2. Norway, Australia, North Carolina.

Fergusonite, $E_2O_3 \cdot (CbTa)_2O_5$ with Th, Zr, U, Fe, and Ca. Ce = 0.5–13 per cent; Y = 27.9 – 47.1 per cent; $ThO_2 + ZrO_2$ = 0–7 per cent. Norway, Australia, Texas.

Samarskite, $(Fe, Ca, UO_2)_3 E_2 ((Cb, Ta)_6O_{21}$, contains Ce = 1.2–6.4 per cent; Y = 4.72–21.2; $ThO_2 + ZrO_2$ = 0–7 per cent. Ural Mountains, North Carolina.

Monazite, EPO_4 with Th, SiO_2, etc., Ce = 49–74 per cent; Y = 0–7.6 per cent; ThO_2 = 1–20 per cent. Brazil, Carolinas, Idaho, Ceylon, India, etc. (See Mantle Industry under Thorium.)

Cerite, basic silicate, $H_3(CaFe)Ce_3Si_3O_{13}$, contains Ce = 50.7–71.8; Y = 0–7.6; ZrO_2 = 0–11.7 per cent. Sweden, Caucasus.

Orthite or *Allanite*, a hydrated silicate, essentially $H_2O \cdot 4(Ca, Fe'', Be)O \cdot 3(AlFe'''E)_2O_3 \cdot 6\,SiO_2$. Ce = 3.6–51 per cent; Y = 0 – 8 per cent; ThO_2 = 0 – 3.5 per cent. Widely distributed in Greenland and Scandinavia.

Yttrocerite, $Ca_3E_2F_{12} \cdot 1\frac{1}{2}\,H_2O$, contains Ce = 9.3–18.2; Y = 8.1–29.4 per cent. Scandinavia.

The examples given include typical minerals, which are of interest mainly for their rare earth content. In addition to

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[1] See Levy, *The Rare Earths*, pp. 7–89.

[2] In the formulas for minerals Y is to be understood as representing yttrium group elements, and Ce, cerium group elements.

these, many minerals contain appreciable amounts of rare earth elements but are themselves of value chiefly for some other constituent. Among such minerals may be mentioned baddeleyite, columbite, ilmenite, polycrase, rutile, tantalite, thorite, thorianite, titanite, and zircon. Nearly all the minerals of the radioactive elements also contain small amounts of rare earth materials. Since most of the typical rare earth minerals are distinctly radioactive, it has been suggested that there must be some relationship between these two groups of elements. No definite relationship has as yet been established.

Extraction. — The method selected for the extraction of rare earth material from its ores depends on the nature of the ore itself, the presence or absence of certain related elements and the particular purpose for which the extraction is to be made. The following discussion must be considered general in scope and by no means exhaustive.[1]

The ore is ground to a fine powder and extracted with acid or fused. The acid used is generally HCl or H_2SO_4, although HF is sometimes employed. The fusion mixture may be $KHSO_4$, NaOH, or KHF_2. The use of HF or KHF_2 is generally limited to minerals containing considerable amounts of columbium and tantalum. The fluorides of these two elements are soluble, consequently they may be effectively separated from the insoluble rare earth fluorides. The latter may then be decomposed with H_2SO_4.

The solution of rare earth salts is saturated with hydrogen sulfide to remove lead, copper, bismuth, molybdenum, etc., and the rare earths precipitated by adding oxalic acid solution. Separation from the common elements is somewhat more effectively accomplished if both the solutions are boiling hot, the oxalic acid being added slowly while stirring. The crude oxalates are filtered and thoroughly washed.

If either thorium or zirconium is present in any amount, it is usually removed at this point by boiling the crude oxalates with $(NH_4)_2C_2O_4$, which dissolves all the zirconium and most of the thorium.[2] Some rare earth oxalates are dissolved slightly,

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[1] For more detailed discussions see such works as Levy, *The Rare Earths;* Spencer, *The Metals of the Rare Earths;* Böhm's *Darstellung der seltenen Erden*, vol. i.

[2] Many other methods have been used for removing thorium, such as the use of H_2O_2, $Na_2S_2O_4$, $PbCO_3$, or precipitation as sebacate, fumarate, metanitrobenzoate or iodate.

but for the most part they remain undissolved. Thorium may be completely removed from the rare earths by repeated treatment with $(NH_4)_2C_2O_4$ or by precipitation from a neutral or very slightly acid solution with H_2O_2. The white precipitate so formed is a good qualitative test for thorium.

Separation. — After the removal of columbium, tantalum, thorium, and other elements which might interfere with the separation of rare earth elements from each other, the next step is usually the separation of the material into cerium group earths and yttrium group earths. This is best accomplished by the James method as follows: Mix the dried oxalates with enough H_2SO_4 to form a thick paste, then ignite cautiously to expel the excess acid. Dissolve the anhydrous sulfates formed in this manner in ice water and sift in solid Na_2SO_4 or K_2SO_4. The former is usually less expensive, but more is required to give a saturated solution. The order of precipitation is approximately scandium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, yttrium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. The sodium earth sulfates of the first six elements are difficultly soluble, and these are sometimes separated and designated as the cerium group elements. The double sulfates of europium, gadolinium, and terbium are slightly soluble, and these are designated as the terbium group. The double sulfates of yttrium and the elements following it in the above list are very soluble. These are called the yttrium group elements. Usually the sulfate separation is used to divide the rare earth elements into the two groups known as the cerium and yttrium groups. In this case the division takes place at gadolinium, which is found partly in one sub-group and partly in the other.

The separation into groups cannot be made sharply because the yttrium group elements begin to come down before all the cerium group has been precipitated. Consequently, to obtain the cerium group free from the yttrium group, much of the former must be left in solution; likewise to precipitate completely all the cerium group enough alkali sulfate must be added to cause the precipitation of a considerable amount of the yttrium group. Consequently, the amount of alkali sulfate added will depend on whether the object is the elimination of the cerium or the yttrium group.

If the purpose in mind is the purification of some members of the yttrium group, it is generally desirable to remove all of the element cerium with the alkali sulfate. If allowed to remain in solution, cerium distributes itself among nearly all the fractions of the yttrium group and complicates the separations further on. To be sure all the cerium is precipitated it is a good practice to continue adding Na_2SO_4 as long as the neodymium absorption lines can be seen in the solution. When these are no longer visible it is certain that cerium is practically all removed.

For some purposes the presence of cerium in the yttrium group fractions is not objectionable and need occasion no concern, because it is easily removed by the following treatment, which is as nearly quantitative as any operation in the rare earth group: Make the nitrate solution from which cerium is to be removed neutral and add $CaCO_3$ in small pieces to keep it neutral; then add $KBrO_3$ and boil. The cerium is oxidized to the quadrivalent condition and precipitates as a basic salt. Similar oxidation is also accomplished by the use of $KMnO_4$.

If the object of the separation is the purification of the cerium group, the main purpose in the removal of the yttrium group is to prevent the interference of these elements with the fractional crystallization of the cerium group, for the yttrium group if present in considerable quantities will prevent the crystallization of the more soluble members of the cerium group. As a consequence of this situation, if the crude oxalates from the mineral contain less than 20 per cent yttrium earths, it is advisable to omit the Na_2SO_4 treatment and proceed at once with the fractional crystallization of the nitrates. Then the yttrium elements collect toward the soluble end of the series and when they become abundant enough to interfere with the crystallization of the members of the cerium group the Na_2SO_4 separation should be used.

The rare earth elements resemble each other so closely that the ordinary means of separation are of no avail. The methods used in rare earth work are of two general kinds: (1) those depending on the differences in solubilities of the various salts, and (2) those based upon the differences in the basicity of elements. Table XIX shows some of the differences between the members of the rare earth group. The order in which the ele-

TABLE XIX

General Comparison of Rare Earth Group

Elements	Sc	Y	La	Ce	Pr	Nd	—	Sa	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ct
Atomic Numbers	21	39	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72
Atomic Weights	45.1	89.3	139[1]	140.2	140.9	144.3	—	150.4	152	157.3	159.2	162.5	163.5	167.7	169.9	173.5	175	—

Order of Decreasing Abundance	Ce, Nd, La, Y, Sa, Gd, Pr, Er, Yb, Lu, Dy, Ho, Tm, Tb, Eu
General Order of Increasing Solubilities of Salts	La, Ce, Pr, Nd, Sa, Eu, Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Ct
Decreasing Basicity	La, Ce^{III}, Pr, Nd, Gd, Sa, Y, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ct, Sc, Ce^{IV}
Decreasing Heats of Dissociation of Anhydrous Sulfates	La, Y, Lu, Yb, Er, Pr, Nd, Gd, Sa, Sc, Ce
Decreasing Stability of Nitrates	Y, Gd, Tb, Tm, Ho, Er, Yb, Sc
Increasing Volatility of the Chlorides	Yb, Lu, Ct, Sc, Th
Increasing Hardness	Pb, Sn, Ce, La, Zn, Nd, Pr, Sa

Coefficient of Magnetization $X \times 10^{-6}$	Sc	Y	La	Ct	Sa	Nd	Eu	Yb	Gd	Er	Tb	Dy
	−0.05	−0.14	−0.18	about −4.1	−6.5	−33.5	−33.5	+33.6	−161	−189	−237	−290

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[1] Baxter, Tani and Chapin give lanthanum an atomic weight 138.91. *Jour. Am. Chem. Soc.* **43** 1080 (1921), and **44** 328 (1922); Hopkins and Driggs find 138.89 *Ibid.*, **44** 1927 (1922).

ments arrange themselves in the solubilities of their salts will vary somewhat with the different salts and the order of basicity varies slightly, but in general the order is that shown in the table.

The method of fractional crystallization is used to separate members of the rare earth group from each other. It depends upon the fact that analogous compounds of the elements have slightly different solubilities. This method is carried out by the use of various salts and a variety of solvents. Its general principle may be illustrated in this manner: If we have a saturated solution of a mixture of salts of differing solubility and evaporate $\frac{1}{10}$ of the solvent, $\frac{1}{10}$ of the solute will crystallize; the crystals will be composed largely of the least soluble members of the mixture, while the mother liquor will contain nearly all the more soluble salts. If, now, the crystals are dissolved in enough solvent to form a saturated solution, then again partly evaporated, a new crop of crystals is formed more nearly pure than the first. By adding the second mother liquor to the first and repeating the partial evaporation, another crop of crystals is produced. By continuing in this fashion adding the mother liquor from each fraction to the next more soluble portion, the original mixture may finally be separated into a series of fractions, each one differing from its neighbors. Sharp separations are difficult by this method and impossible if the differences in solubilities are slight. As applied to rare earth mixtures, thousands of crystallizations are necessary and at best the separations are not quantitative. It is evident that the end fractions are more easily purified than the intermediate ones. If the salts are quite soluble, the least soluble one of the mixture will be most easily purified.

Methods depending on the differences in basicity are of several types, such as fractional precipitation, fractional decomposition, etc. As an illustration of the method of fractional precipitation we may consider adding a precipitant like NH_4OH to a solution of a mixture of salts. If only a small amount of ammonia is added, the precipitate will contain more of the less basic constituents than the mother liquid. If the precipitate is filtered out and more ammonia added to the filtrate, another precipitate may be obtained. By proceeding in this fashion, the mixture may be separated into any desired number of fractions in which there may be noted a progressive degree of basicity. Separations by these methods are perhaps less tedious than by fractional crystallization, but they usually involve more work and are never quantitative.

Fractional decomposition depends on the fact that if the rare earth salts of oxy-acids are heated they form basic salts which are difficultly soluble. The ease with which this change takes place depends upon the basicity of the element. Accordingly, if a mixture of nitrates is heated gently, the molecules containing the less basic metal are changed to the insoluble basic nitrate first. As usually carried out the mixed nitrates are heated in a casserole to the desired temperature, poured out on a marble slab, taken up with water, and the insoluble material filtered out. By dissolving the basic salt in HNO_3 the process may be repeated and a series of fractions obtained similar to those formed by fractional crystallizations.

It is evident from the principles upon which these fractional methods are based that only by long continued repetition can anything like a pure product be obtained. In very few cases will a single method suffice to yield a pure compound. Almost always the worker is required to select a combination by which the desired element is separated first from one neighbor, then from another.

It is to be observed that any fractionation method is wasteful of material. When it is considered that the original ore contains only a small per cent of mixed rare earths; that of this mixture only a small per cent of a certain element is present; that in the purification of that element thousands of fractionations are necessary; and that at each step some of the desired material is lost — when these facts are considered, we can understand why the chemistry of this group has developed slowly. Large quantities of expensive materials are required and a tremendous investment of time and labor is involved.

As any method of fractionation continues it is essential to watch the composition of the fractions in order to know what effect the treatment is producing. This is done in several ways: (1) By change in color; this is only an approximate method satisfactory means of testing the purity of any material. The method selected for determining the atomic weights should give good comparative results, but need not give absolute values. Obviously this manner of controlling fractionations is tedious, but it gives splendid results except in such a case as an element that is mixed with two impurities, one of lighter and the other of heavier atomic weight. (3) Usually the most satisfactory means of controlling fractionation is by spectral analysis. Commonly a small direct-vision spectroscope is sufficient to give a very accurate idea of those constituents of a solution which have absorption lines in the visible portion of the spectrum. Photographic examination of the arc, spark, or flame spectra gives the most accurate and most critical data concerning the purity of any material. (4) Another method of estimating the relative composition of a mixture of two oxides is by means of the magnetic susceptibility. The rare earth elements differ more widely from one another in their magnetic properties than in any other way, consequently this method is capable of accurate and efficient use in controlling the system of fractionation. After the apparatus has been once adjusted, determinations may be made rapidly and accurately.

Separation of the Cerium Group. The best method for the preliminary separation of the members of the cerium group from each other is the fractional crystallization of the double magnesium nitrate of the formula $2\ E(NO_3)_3 \cdot 3\ Mg(NO_3)_2 \cdot 24\ H_2O$. The cerium group nitrates are mixed with the calculated amount of $Mg(NO_3)_2$ and subjected to fractional crystallization. After some time it is noticed that the fractions begin to develop distinct colors as the crystallization progresses. The elements crystallize out in the order shown in Table XX, which gives also the atomic weights and the colors of the salts. The fractional crystallization of the double nitrates does not give sharp separations and cannot be used alone for the purification of these salts. But the separation of neodymium and samarium in this way is fairly satisfactory. A glance at the table shows the rather remarkable fact that the order of increasing solubility is exactly the order of increasing atomic weights.

Lanthanum is one of the most easily purified members of the rare earth group because it is the most basic of all the group and because its salts are the least soluble. Pure lanthanum

TABLE XX

Cerium Group

ORDER OF INCREASING SOLUBILITIES OF THE DOUBLE NITRATES						
La 139 No color	Ce 140.25 ous No color ic Orange to Red	Pr 140.6 Green	Nd 144.3 Red to Violet	Sa 150.4 Topaz Yellow	Eu 152 Faint Rose	157.3 No color

material may be obtained by the long-continued fractionation of the double magnesium nitrate or the double ammonium nitrate; other methods used effectively are: (1) the double potassium carbonate, after the removal of cerium; (2) saturate ice water with impure $La_2(SO_4)_3$, then warm gradually to 32°, when pure lanthanum sulfate crystallizes out.

Praseodymium is difficult to obtain in pure compounds both because of its scarcity and close resemblance to other elements. The best methods of separation are as follows: (1) Set out from a double magnesium nitrate series such fractions as contain only lanthanum and praseodymium; continue the fractionation of the same salt or of double ammonium nitrate. Praseodymium appears at the soluble end, but usually neodymium appears there also, even if its presence is unsuspected at first. (2) Remove from the magnesium double nitrate series the fractions which contain only praseodymium and neodymium and continue the fractionation as the manganese double nitrate, when praseodymium separates in the least soluble portions. Other methods used are: Crystallization of the oxalates from nitric acid; of the double ammonium nitrate or double carbonate.

Neodymium, being one of the more abundant rare earth metals, is more easily obtained in pure compounds. The last impurity to be removed is usually praseodymium, which is separated by the methods already given. The following methods are also valuable: Fractionation of the meta-nitrobenzoate, of the simple nitrates in strong nitric acid, or the fractional precipitation of the chloride by HCl gas.

If the magnesium double nitrate fractions containing samarium, europium, and gadolinium contain also appreciable quantities of the yttrium group earths, crystallization does not take place well. Where trouble of this sort occurs in the soluble end of a cerium group fractionation, it becomes necessary to repeat the yttrium group separation before attempting to purify samarium, europium, or gadolinium.

Samarium may be almost quantitatively separated from neodymium by a simple continuation of the magnesium double nitrate crystallization. From europium and gadolinium it may be separated by adding to the series some bismuth nitrate and continuing the fractionation. The bismuth salt is isomorphous with the rare earth salts and is intermediate in solubility between samarium and europium. In this manner samarium crystallizes in the less soluble portions and bismuth is removed from it by hydrogen sulfide. The fractional crystallization of a dimethylphosphate series or a double manganese nitrate series in nitric acid is also efficient.

Europium is one of the rarest members of the rare earth group. Its lines in the arc spectrum are particularly intense, so minute amounts of the element may be detected.[1] Its separation is particularly difficult and requires a very large amount of material. In the magnesium double nitrate fractionation it collects in the samarium fractions, from which it may be removed by the fractionation with bismuth nitrate.

Gadolinium may be obtained from the most soluble fractions of the magnesium double nitrate series, especially if europium is absent and bismuth nitrate is added. It may also be obtained: (1) at the insoluble end of a double nickel nitrate series; (2) by the crystallization of the simple nitrate in 30 per cent HNO_3; and (3) at the insoluble end of a bromate series.

Separation of the Yttrium Group. — Before an attempt is made to separate the yttrium group elements from each other, it is usually advisable to see that all cerium has been removed. The first step in separating the yttrium metals from one another is effectively accomplished by means of the fractional crystallization of the bromates. The yttrium group sulfates are treated with barium bromate and the precipitated $BaSO_4$ filtered out.

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[1] See "Absorption Spectrum of Samarium and Europium," *Zeit. anorg. Chem.* 116 96 (1921).

As the crystallization of the bromates continues the elements arrange themselves in the order shown in Table XXI, which places the least soluble first. The atomic weights and predominating colors of the salts are also shown. Again there is a strikingly close relationship between the order of solubilities and the increasing atomic weights. The noticeable exceptions in the case of yttrium and scandium have led to the suggestion that these elements should not be considered as typical members of the rare earth group.

TABLE XXI

Yttrium Group

ORDER OF INCREASING SOLUBILITY OF YTTRIUM GROUP

Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu	Ct	Sc
157.3	159.2	162.5	163.5	89	167.7	169.9	172	174	(?)	45.1
None	None	Bright Green	Yellow to Orange	None	Deep Rose	Blue Green	None	None	None	None

Terbium is found in rare earth material in exceedingly small amounts and its purification is unusually difficult. For the complete separation of terbium from other elements, several steps are necessary. After a long fractionation of a bromate series, the terbium fractions are best subjected first to fractional crystallization of the nitrate from nitric acid in the presence of bismuth nitrate, then by crystallization of the double nickel nitrates, and finally by fractional precipitation with ammonia.

Dysprosium in a fairly pure state may be prepared by long continued fractionation of a bromate series alone. More rapid results and probably a more nearly pure product is obtained by the fractionation of a simple nitrate series, a double bismuth nitrate series, or an ethyl sulfate series.

Holmium is one of the more rare elements and it is a particularly difficult one to obtain in pure form, on which account its individuality is still somewhat doubtful. The purification involves several steps, such as crystallization of the *m*-nitrobenzene sulfonates, of the simple nitrates, of the double ammonium oxalates, and finally fractional precipitation with ammonia. Concentration of holmium may also be accomplished by using an ethyl sulfate series, fractional precipitation by sodium nitrite and especially fractional decomposition of the nitrate.

Yttrium is one of the most abundant rare earth elements and its purification is easily accomplished. Yttrium fractions from a bromate series are freed from dysprosium, holmium, and erbium by fractional precipitation with ammonia, K_2CrO_4, or $NaNO_2$. The latter is probably the most effective. Yttrium salts give no absorption lines in the visible portion of the spectrum, consequently the removal of holmium and erbium is easily observed by the direct vision spectroscope.

Erbium may be prepared from the erbium-yttrium fractions of a bromate series by methods similar to those used in purifying yttrium, except that erbium is concentrated in the less basic fractions. Fusion of the nitrates gives a rapid separation of these two elements.

Thulium in a fairly pure state may be obtained by the long-continued fractionation of a bromate series. The separation of erbium and thulium is fairly satisfactory by this method alone. According to Welsbach [1] thulium is a mixture of three elements which he designated as thulium I, II, and III. Probably no better thulium material has ever been obtained than that prepared by James [2] using the bromate method, which gave a homogeneous product after 15,000 operations.

The difficulty experienced in the preparation of pure thulium illustrates the fact that separations are extremely difficult from the soluble end of a bromate series unless an element differs noticeably in basicity from its neighbors.

Ytterbium (or neo-ytterbium) may be separated from lutecium by the fractional crystallization of the ammonium double oxalates in concentrated ammonium oxalate; or by the fractional crystallization of the nitrates in nitric acids; or by the difference in the volatility of their chlorides.

Celtium was isolated from the soluble end of a series from gadolinite by fractional crystallization of the nitrates in nitric acid. Its compounds have properties intermediate between those of scandium and lutecium. Its atomic weight has not been determined, but the atomic number 72 has been assigned to this element. The discovery of hafnium, a close relative of

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[1] *Zeit. anorg. Chem.* **71** 439 (1911).

[2] *Jour. Am. Chem. Soc.* **33** 1333 (1911).

zirconium of atomic number 72, has raised a question concerning the existence of celtium.

Lutecium (called by Welsbach cassiopeium) may be separated from the old ytterbium by the fractional crystallization of the nitrates, the double oxalates or the bromates, in each case the lutecium salts being more soluble.

Scandium is usually present in rare earth minerals in small amounts (the rare mineral thortveitite containing 37 per cent Sc_2O_3 is an exception). It collects in the soluble end of the bromate fractionations, but it is easily separated from the other soluble salts by the fact that it is the least basic of the whole group. Consequently, fractional precipitation or fusion of the nitrates concentrates the scandium rapidly. Scandium may also be precipitated from boiling acid solution by sodium silicofluoride; its double ammonium tartrate and double potassium sulfate are also difficultly soluble.

Metallurgy. — The metals of most of the cerium group elements have been prepared, three general methods having been used: (1) fusion of the anhydrous halides with sodium, potassium, calcium, or aluminium; (2) electrolysis of the fused chlorides or of a solution of the oxide in the molten fluoride; (3) heating the oxides with magnesium, calcium, or silicon. Reduction with aluminium has also been tried, but it is not satisfactory except possibly for cerium itself. Electrolysis has been the most successful, the other methods usually giving at best an alloy.

The yttrium group metals have never been prepared in pure form. Impure yttrium has been prepared by methods similar to those used in preparing the cerium group metals, and a mixture of yttrium group metals has been made by action of finely divided sodium upon the metallic oxides. The difficulties in the way of preparing the yttrium group metals are mainly two: The metals have much higher melting points than the cerium group metals; and (2) the chlorides are easily volatile. Reference to Table XXII will show that in the cerium group the melting points of the elements and the chlorides are of the same order of magnitude; while in the case of the yttrium group elements, the metals melt at a much higher temperature than the chlorides. Hence, any method involving the fused chlorides is difficult or impossible because of the freezing of the bath.

Table XXII

Properties of Rare Earth Metals

	Color	Melting Point	Melting Point of Chlorides	Sp. Gr.	Heat of Formation per Equiv. Wt. of Oxide in Calories	Coefficient of Magnetization of Oxide × 10^{-6}
Lanthanum	White	810	907	6.1545	74,100	−0.18
Cerium	Gray	623	848	7.0242	56,100	
Praseodymium	Yellow	940	818	6.4754	68,700	
Neodymium	Slightly Yellow	840	785	6.9563	72,500	33.5
Samarium	Pale Gray	1350	686	7.7–7.8		6.5
Yttrium		1250	680			
Dysprosium			680			290
Erbium		1250(?)				
Ytterbium		About 1800	880			

Electrolysis of the fused mixture of the rare earth chlorides is a process of considerable commercial importance producing what is called misch metal. (See Chapter X, pp. 170–172.)

Properties. — Cerium group metals resemble each other closely both in physical and chemical properties. They are white or slightly yellowish in color, moderately stable in dry air, but tarnishing in moist air, lanthanum oxidizing most easily. Compared with some common elements they may be arranged in the order of increasing hardness as follows: lead, tin, cerium, lanthanum, zinc, neodymium, praseodymium, and samarium. Cerium may easily be cut with a knife while samarium has a hardness comparable with steel. They decompose water slowly in the cold, quite rapidly at the boiling temperature, hydrogen being evolved. At higher temperatures they show great affinity for oxygen. Their oxides have heats of formation comparable to those of alumina and magnesia. Hence, they are powerful reducing agents. They dissolve in dilute acids easily and in general they unite directly with hydrogen, nitrogen, the halogens, sulfur, and phosphorus. They alloy readily with such metals as magnesium, zinc, aluminium, and iron.

Uses. — Few uses have as yet been found for the rare earth metals or their compounds. A mixture of the metals containing roughly 50 per cent cerium is used under the name misch metal. (See p. 168.) Compounds of neodymium and praseodymium find a limited use in ceramics, where they are used to produce certain color effects. Neodymium phosphate produces[1] an amethyst red color in porcelain, while the praseodymium salt produces a bright green, and various mixtures give many beautiful shades. The oxides of the same metals are used in the manufacture of blue optical glass. Neodymium tungstate produces a bluish red color in porcelain. A mixture of neodymium and praseodymium nitrates is used for stamping the trade mark on incandescent gas mantles. (See p. 188.) The salicylate of these elements is sold under the trade name "Dymal" as a soothing antiseptic dressing for wounds.

Compounds. — A surprisingly large number of compounds of the rare earth elements has been prepared. This is probably due to the persistent effort to find combinations which would permit easier and more efficient separations than the cumbersome fractionations which have always been used. The most important compounds are enumerated in the following summary: —

Oxides of the type R_2O_3 are formed by all rare earth elements, by the ignition of the hydroxide, nitrate, sulfate, carbonate, or oxalate. In general the basicity decreases with increase of atomic weight, though yttrium and scandium are exceptions to the rule. The basicity of lanthanum approaches that of the alkaline earths, while scandium is about as basic as aluminium.

Cerium forms the oxide CeO_2, which is more stable than Ce_2O_3; the series of ceric salts are well defined and stable compounds. Both praseodymium and terbium give higher oxides but neither of these forms a series of salts. Terbium peroxide has a brownish black color and is the most highly colored compound of the group.

The *hydroxides* are precipitated in a gelatinous mass by the action of the alkalies upon the hot solutions. If the alkaline solution is added to a rare earth in the cold, the precipitate is usually a basic salt or a mixture of the hydroxide and basic salt. The hydroxides are not soluble in excess of reagent, but dissolve readily in acids and generally absorb carbon dioxide from the air.

Sulfides R_2S_3 may be formed by the reduction of the sulfates or by the action of H_2S gas on the hot oxides. They are not formed in solution.

Carbides RC_2 are prepared by reduction of the oxides by carbon in the electric furnace. When moistened, the carbides give a complex mixture of gases, of which acetylene, hydrogen, ethylene, and ethane are the most prominent.

Halogen compounds are soluble except the fluorides. The chlorides,

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[1] *Ber. deut. Keram. Ges.* **1**, part. 1, 24 (1920).

the best known, are easily prepared by dissolving the hydroxides, ca bonates, oxides, or, in some cases, oxalates in HCl. They form crysta of the formula $RCl_3 \cdot 6 H_2O$ (an exception is praseodymium which giv $PrCl_3 \cdot 7 H_2O$). Basic chlorides are obtained by heating the hydrates to temperature around 120° C., but if the heating is done cautiously in atmosphere of HCl, the anhydrous salts are obtained. The chlorides sho little tendency to form double salts with other metallic chlorides.

Cyanides of the simple type are unknown. The addition of KCN to rare earth solution precipitates the hydroxide. Double cyanides a sometimes used in separations of rare earth mixtures. For example, wh $K_4Fe(CN)_6$ is added to a solution containing yttrium $KYFe(CN)_6 \cdot 3 H_2O$ precipitated as a gelatinous mass.

Chlorates of the yttrium group only have been prepared, best by addi $E_2(SO_4)_3$ to $Ba(ClO_3)_2$, when there is formed a hydrate of the formu $E(ClO_3)_3 \cdot 8 H_2O$. The bromates are similar and are of great service in t yttrium group separations.

Sulfates are formed with varying amounts of water of crystallizatio For example $Ce_2(SO_4)_3$ forms hydrates with 12, 9, 8, 5, or 4 molecules water. The solubility of the sulfates decreases with rise of temperature a fact utilized in fractionation and separation of rare earths from oth elements.

Acid sulfates are formed by using an excess of acid and on heating the normal sulfates are formed. It is doubtful if all the excess acid can expelled without partial decomposition of the normal sulfates. Bas salts of the type $R_2O_3 \cdot SO_3$ are formed by heating the normal sulfat These reactions are of much importance because many rare earth ator weights have been determined by the use of the sulfates.

The double alkali sulfates are used in separating the yttrium and ceri groups. The ethyl sulfates are very useful in certain separations, but th are rather difficult to form and they must be handled very carefully becau they decompose easily, even at room temperature. Sulfites, thiosulfat dithionates, selenites, and selenates of most of the metals have been p pared.

Nitrates of the cerium group, $R(NO_3)_3 \cdot 6 H_2O$, are crystalline but th of the yttrium group, which contain 3 or 5 molecules of water, are r easily obtained in crystalline form. These salts are deliquescent, solub in both water and alcohol, but difficultly soluble in HNO_3. The solubili in HNO_3 is greatest in lanthanum, diminishes to a minimum in gadolini and then increases again. This fact is very useful for certain fractionatio

Basic nitrates, insoluble in water but decomposed by acids, are form by heating the nitrates. This behavior is of great importance in separation of certain elements.

Double nitrates of the cerium group are easily crystallized. Th stability decreases gradually with rise of atomic weight of the metal, a in the yttrium group crystalline double nitrates do not form. Co sequently, the use of the double nitrates in fractionation is limited to cerium group.

Phosphates are precipitated as a gelatinous mass when a solution of ph phoric acid or alkaline phosphates is added to a solution of rare earth salts. The phosphates, especially the complex salts, are found frequently in nature. For example, monazite and xenotime are orthophosphates.

Carbonates are formed by passing carbon dioxide into a suspension of earth hydroxides or by adding an alkaline carbonate to a neutral rare earth solution.

Basic carbonates and double carbonates are formed by some of the rare earth metals. The stability and solubility of the latter class of compounds increases with increasing atomic weight of the rare earth metal. Both the sodium and ammonium double carbonates are less soluble than the corresponding potassium compounds. These salts are likewise useful in fractionations.

Oxalates are of prime importance because of the fact that the rare earth oxalates are insoluble in acids. Hence, the addition of oxalic acid to a solution containing rare earth salts and free mineral acid furnishes a convenient method of removing the common metals. The rare earth oxalates, however, absorb many salts from the mother liquor, and repeated precipitation is necessary to remove the alkali and alkaline earth elements. Best results are obtained by bringing the solutions together at a boiling temperature and stirring vigorously as the solutions are mixed. A large number of precipitations will remove all but traces of the alkali metals, but one or two precipitations with ammonium sebacate will accomplish the same result more quickly.

Double alkali oxalates are formed by the elements of the yttrium group.

In addition to the compounds listed in the foregoing tabulation a very large number of salts of the rare earth elements have been prepared and more or less thoroughly studied with respect to their usefulness in the separation of the rare earths. Among these salts of minor interest may be enumerated the following: chromates, molybdates, tungstates, uranates, columbates, formates, acetates, tartrates, benzoates, succinates, hippurates, citrates, glycollates, cacodylates, and phthalates.

CHAPTER VII

GROUP III — GALLIUM, INDIUM, THALLIUM

THE metals of the aluminium sub-group are permanent in the air at ordinary temperatures, but when heated in oxygen or the air they become coated with their oxide. The volatility of the metals increases with the atomic weights, and the heavier metals are more easily reduced than those of lower atomic weight. The metals are all malleable, fusible, have small atomic volumes and form hydroxides, $M(OH)_3$, which are typically amphoteric in the first three elements of the sub-group and basic only in the case of thallium. The last four members of the family form alums, and both aluminium and thallium form organo-metallic compounds, resembling zinc in this respect.

The typical valence in this sub-group is three, but gallium forms a chloride, $GaCl_2$, while indium forms two sub-chlorides, $InCl_2$ and $InCl$, and thallium forms four chlorides, $TlCl_3$, $TlCl_2$, Tl_2Cl_3, and $TlCl$. Thallium forms a whole series of univalent salts which are more stable and better known than its trivalent series. The thallous compounds resemble the analogous compounds of the alkali metals.

The physical constants of the members of this sub-group are shown in Table XXIII.

TABLE XXIII

Properties of the Aluminium Family

	BORON	ALUMINIUM	GALLIUM	INDIUM	THALLIUM
Atomic Weight	10.9	27.0	70.1	114.8	204.0
Specific Gravity	2.45	2.7	5.9	7.4	11.8
Atomic Volume	4.5	10.0	11.8	15.5	17.3
Melting Point	Above 2000°	657°	30°	176°	285°

GALLIUM

Historical. — Special interest attaches to the history of gallium because its existence, properties, and compounds were predicted by Mendeléeff.

Within five years after he had made an extended list of the properties to be expected in eka-aluminium and its compounds, the element gallium was discovered. The prompt fulfillment of the prophecy did much to strengthen faith in Mendeléeff's generalization.

Lecoq de Boisbaudran, while examining some zinc blende from the Pyrenees in 1875, discovered two new lines in the violet of the spectrum. This led to the identification of the new element, for which the discoverer suggested the name gallium, after the old name for France.

Occurrence. — Gallium has been found to be widely distributed in nature but always in small amounts. The richest source known is a certain English iron ore which is said to contain 1 part in 33,000. Another one of the principal sources is the Bensberg sphalerite, which contains 0.016 gram per kilogram. It is present in zinc ore generally, in some pyrite deposits, and manganese ores and in many iron ores, especially magnetite, but not siderite; it is said to be a constant constituent of bauxite ores and generally of kaolin. It has been detected in certain mineral waters of France, and its presence in the sun's atmosphere has been shown. The principal source of gallium in the United States has been from the zinc deposits of Oklahoma.[1] During the war the high price obtained for pure zinc encouraged the redistillation of the spelter. In this process a small residue was obtained representing 0.5 per cent of the spelter. The residue was largely lead from which a small amount of a gallium-indium alloy was separated by sweating. From this material much of our recent information on both gallium and indium was obtained.

Extraction.[2] — (*a*) To extract gallium from an ore, the material is ground to a fine powder, dissolved in aqua regia, and the excess acid expelled by heating. Cool, add zinc, and filter off the precipitated metals, then boil for a long time with zinc, when a basic gallium salt is precipitated along with aluminium, iron, zinc, etc.

(*b*) From a lead residue, gallium and indium may be extracted by dissolving the material in nitric acid, and evaporating to dryness. Add 1 : 1 sulfuric acid to form lead sulfate; then filter and add NH_4Cl and NH_4OH, which precipitates the hydroxides of gallium and indium.

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[1] *Jour. Ind. and Eng. Chem.* **8** 225 (1916); *Am. Jour. Sci.* **41** 351 (1916).

[2] See Dennis and Bridgman, *Jour. Am. Chem. Soc.* **40** 1531 (1918); Richards and others, *Jour. Am. Chem. Soc.* **41** 131 and 133 (1919); Porter and Browning, *Jour. Am. Chem. Soc.* **41** 1491 (1919).

(c) From zinc flue dust both gallium and germanium may be obtained[1] by dissolving the material in an excess of commercial HCl, adding a little $KClO_3$ and distilling. Germanium distills over and gallium may be separated from the remaining solution.

Purification. — Since gallium is not precipitated by H_2S in acid solution it is easily separated from lead, copper, mercury, and arsenic. It is separated from nickel, cobalt, zinc, manganese, and the alkaline earths by the fact that it is precipitated by NH_4OH in the presence of NH_4Cl. It is freed from iron, titanium, thallic compounds, uranium, indium, and the rare earths by the solubility of its hydroxide in NaOH. Chromium and vanadium may be removed by means of oxidizing agents. Gallium is separated from aluminium, chromium, and beryllium by the addition of $K_4Fe(CN)_6$ to a solution containing much HCl, when $Ga_4(Fe(CN)_6)_3$ is precipitated. From the ferrocyanide the gallium may be recovered by (1) dissolving in alkali and bubbling in CO_2, when a basic gallium carbonate precipitates; or, (2) if zinc is absent, the ferrocyanide may be oxidized to ferricyanide by H_2O_2 in alkaline solution, then NH_4Cl and NH_4OH added. The precipitated $Ga(OH)_3$ is free from cyanides.[2]

The separation of zinc and gallium may be accomplished by precipitating $Ga(OH)_3$ with NH_4OH in the presence of NH_4Cl, but the gelatinous precipitate adheres badly to the side of the dish, filters slowly and occludes zinc salts. Another method of separating gallium and zinc is to precipitate the latter with potassium mercuric thiocyanate, then precipitate the excess mercury with H_2S and the gallium with Na_2SO_3 in the presence of HCl. Gallium may be separated from a small amount of zinc by adding $NaHSO_3$ or NH_4HSO_3 to a neutral or slightly acid solution and boiling, when the gallium is precipitated.

Gallium and indium may be separated by the solubility of $Ga(OH)_3$ in an excess of NaOH or KOH,[3] by passing a current through a solution of their salts, indium separating first; and also by fractional crystallization of the ammonium gallium-

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[1] Fogg and James, *Jour. Am. Chem. Soc.* 41 947 (1919).

[2] Porter and Browning, *Jour. Am. Chem. Soc.* 43 111 (1921).

[3] This method does not remove all the indium. Richards and Boyer, *Jour. Am. Chem. Soc.* 41 133 (1919).

ms, the gallium separating at the insoluble end. It
d also that gallium and indium metals may be sepa-
rolonged heating at 1800°. Gallium, indium, and
separated by fractional distillation of their chlorides.
s at 215 220°, but it may be sublimed in a vacuum
rature as low as 65 80°; $InCl_3$ begins to volatilize
l distills rather slowly at 600°; $ZnCl_2$ boils at 730°.
gy. Lecoq de Boisbaudran exhibited, at the Paris
in 1878, 62 grams of metallic gallium which he had
rom 2400 kilograms of zinc blende. His method of
was the electrolysis of an alkaline solution of a gal-
This is still the best known method of producing
t. Sometimes the metal collects on the platinum
n the liquid state and sometimes in the solid, as a
ntact with the solid phase does not always start the
he tree, but cooling the bath with ice causes the tree
The trees formed on the cathode are hard and stable
hey are kept at least 10° below the melting point.
es. — Metallic gallium is gray or white, but shows a
on its bright surface. It is a brilliant, diamagnetic
a striking metallic luster, forming a splendid reflec-
, however, tarnishes quickly. It is tough, but soft
be cut with a knife. Its melting point as determined
ls is 30°.8, which is somewhat higher than previous
ions. The latent heat of fusion is 19.03 calories
of metal. Molten gallium resembles mercury in
, and the metal has the ability of remaining liquid
gh it is undercooled as much as 30°. Gallium ex-
solidifying. It has been suggested that this prop-
to the presence of impurities, but the most careful
Richards shows that the solid has a specific gravity
d the liquid of 6.095. The liquid is electro-negative
id. Liquid gallium has a coefficient of compressi-
° of 3.97×10^{-6}, while the solid has a value of 2.09 ×
e compressibility of the liquid is almost identical
of mercury, while the element conforms to the almost
xperience that the compressibility of a solid is less
of its liquid.

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[4] *See Am. Jour. Sci.* 42 (IV), 389 (1916).

[5] *Jour. Am. Chem. Soc.* 43 274 (1921).

Gallium has only slight action upon cold water, but at the boiling temperature the reaction is vigorous.[1] It remains unchanged in the air at ordinary temperatures, but when heated it oxidizes superficially, although it does not burn at red heat. It dissolves in dilute HCl and in NaOH, liberating hydrogen. In HCl the solid goes into solution more quickly than the liquid. Cold dilute nitric acid has little effect upon it, but when warmed the acid attacks the metal slowly. Aqua regia is a splendid solvent, while ammonia dissolves it slowly. It unites rapidly with chlorine, more slowly with bromine, but will not unite with iodine until it is heated.

It alloys readily with aluminium, and these alloys are said to decompose cold water readily. The alloys rich in gallium are liquid. It readily alloys also with indium.

Uses. Gallium has no commercial uses at present. It has been suggested that the gallium-aluminium alloy would form an efficient cathode in a metal vapor lamp.[2] It might also be useful in manufacturing optical mirrors. Its use in high temperature thermometers is not feasible because the liquid wets both glass and quartz.

Probably the most promising suggested use of gallium is in connection with the preparation of a monochromatic lamp. A gallium-cadmium alloy containing 2-3 per cent gallium is distilled at 0.001 mm. pressure into the lamp. Three amperes at 110 volts are consumed, and a pure red light of wave length λ 6439 is produced. The lamps need preheating at the start. The function of the gallium seems to be to soften the cadmium, in order to prevent injury to the lamp when the cadmium solidifies.

Compounds. The compounds of gallium resemble those of aluminium quite closely, although there is considerable evidence of a slightly stronger basicity.

The *oxide* of gallium, Ga_2O_3, is prepared by igniting the hydroxide or nitrate. It is white, infusible at red heat, almost insoluble in both acids and alkalies after it has been strongly ignited. It may be reduced with hydrogen to a supposed suboxide, GaO, or to the metal. When fused with the oxide of samarium or of chromium, it becomes phosphorescent under the influence of the cathode rays.

The *hydroxide*, presumably $Ga(OH)_3$, is precipitated as a white gelati-

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[1] *Am. Jour. Sci.* **42** (IV), 389 (1916).

[2] *Ger. Pat. Zentralblat.* (1910) I 705.

nous mass by ammonia. It is readily soluble in the fixed alkalies and only slightly soluble in excess of ammonia.

The *nitrate*, $Ga(NO_3)_3$, is prepared by dissolving Ga_2O_3 in HNO_3. It is deliquescent and is completely decomposed at 200°, giving the oxide.

The *chlorides*, $GaCl_2$ and $GaCl_3$, are formed. The latter is prepared by heating the metal in hydrogen chloride or chlorine. It is crystalline, deliquescent, and yields a clear solution with a small quantity of water, but a difficultly soluble basic salt with a larger amount of water. The dichloride is formed by the action of the metal on the trichloride.

Gallium forms the bromide and iodide GaX_3 by direct combination of the elements.

The *sulfate*, $Ga_2(SO_4)_3$, is soluble, is not deliquescent, and crystallizes with ammonium, potassium, rubidium, caesium, and thallium (Tl^I) to form alums. The caesium alum is used for the separation of gallium and indium by fractional crystallization as well as for micro-chemical analysis.

The *ferrocyanide*, $Ga_4(Fe(CN)_6)_3$, is precipitated by adding $K_4Fe(CN)_6$ to a gallium solution containing one third its volume of concentrated HCl. This is a characteristic reaction, useful in the separation of gallium and capable of detecting as little as 0.0001 gram of the element.

Detection and Estimation. — Gallium is best detected spectroscopically,[1] the spark spectrum showing two bright lines in the violet, at λ 4171 and λ 4031. By this method 0.003 milligram of gallium may be detected in the presence of 1.63 milligrams of indium. The following are qualitative tests: —

A pure gallium salt is not precipitated by H_2S, but in a faintly acid or ammoniacal solution containing silver, zinc, manganese, or arsenious salts, Ga_2S_3 is completely precipitated along with the other sulfide. Boiling a neutral or slightly acid solution of a gallium salt with $NaHSO_3$ or NH_4HSO_3 produces a precipitate, but indium must be absent and zinc present in not too large a proportion.[2]

$Ga(OH)_3$ is precipitated by NH_4OH, $(NH_4)_2CO_3$, or the carbonates of the alkali or alkaline earth metals, or by boiling with an excess of precipitated cupric hydroxide. The precipitate is soluble in the fixed alkalies.

A delicate test for gallium is the precipitation of $Ga_4(Fe(CN)_6)_3$ by adding $K_4Fe(CN)_6$ to a gallium solution containing 33 per cent by volume of concentrated HCl.

The quantitative estimation of gallium is usually accomplished by precipitating the hydroxide from a pure solution with a slight excess of ammonia, boiling to expel the excess precipitant and finally igniting the hydroxide to Ga_2O_3. Precipitates obtained by adding $NaHSO_3$ or NH_4HSO_3 may also be ignited to Ga_2O_3.

INDIUM

Historical. — In 1863, Reich and Richter were examining some zinc sulfide from Freiberg, when they observed two new blue lines in the spark

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[1] For the arc spectrum of gallium see Uhler and Tanch, *Astrophy J.* **55** 291 (1922).

[2] Porter and Browning, *Jour. Am. Chem. Soc.* **41** 1491 (1919).

spectrum. From the same material they succeeded in separating a new metallic element, for which they proposed the name of indium, signifying indigo blue.

Occurrence. Indium, one of the rarest of metals, is found in minute amounts in a large number of minerals. The amount never exceeds $\frac{1}{10}$ of 1 per cent. It is present in most zinc blendes and tin ores, in some iron ores, especially siderite (distinct from gallium); in some manganese, lead, and tungsten ores; it has also been detected in the atmosphere of the sun. The principal source is flue dust from the zinc smelters, or zinc from indium-bearing blende.

Extraction. Indium may be extracted from zinc by dissolving the metal in a quantity of acid just insufficient to give complete solution. Upon the residue of undissolved zinc there collects on standing a spongy mass, which is composed of lead, copper, cadmium, tin, arsenic, iron, and indium. This mass is collected, washed, dissolved in HNO_3, and evaporated with H_2SO_4. The lead sulfate is filtered off, and the hydroxides of iron and indium precipitated by an excess of NH_4OH. These are dissolved in a small amount of HCl and the solution, which should be nearly neutral, is boiled with an excess of $NaHSO_3$, when indium precipitates as the basic sulfite of the formula, $In_2(SO_3)_3 \cdot In_2(OH)_6 \cdot 5\,H_2O$. This may be dissolved in H_2SO_3 and the indium precipitated by addition of NH_4OH.

Indium and iron may also be separated by adding potassium sulfocyanide to the mixed chlorides in acid solution and extracting the ferric sulfocyanide with ether. Indium may be separated from both aluminium and iron by adding an alcoholic pyridine solution to the chlorides, when $InCl_3 \cdot 3\,C_5H_5N$ is precipitated.

Metallurgy. — Metallic indium may be prepared in a number of ways: (1) heating the oxide with hydrogen; (2) heating the oxide with sodium produces first a brittle alloy from which the sodium is removed by water and fused Na_2CO_3; (3) by adding zinc to a solution of indium compounds; (4) electrolysis of the chloride or sulfate solution in the presence of pyridine, hydroxylamine, or formic acid, a branched tree being formed. The fractional electrolysis of the sulfate solution is the best means of obtaining pure indium.[1] The spongy metal may be dried at 120° and fused in an atmosphere of hydrogen.

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[1] *Jour. Am. Chem. Soc.* 29 485 (1907).

Properties. — Indium is a white metal, softer than lead, easily malleable, ductile, crystalline, and diamagnetic. Its coefficient of expansion is 0.0000459, its specific heat 0.057, its compressibility at 25° 0.0000027, which is about two-thirds that of mercury.

It does not decompose water, even at the boiling temperature. At low temperatures it is stable in the air, but when heated it burns with a blue flame, producing In_2O_3. The heat of combustion is 1044.6 calories per gram of metal. It unites directly with the halogens and with sulfur. It dissolves in mineral acids, but not in KOH solution. In the electromotive series it falls between iron and lead. It forms alloys with lead, thallium, tin, gold, platinum, gallium, mercury, and sodium.

Compounds. — Indium forms compounds similar to those of gallium, but more basic and in some ways suggestive of the compounds of iron. The characteristic valence is 3, but well-defined bivalent and univalent compounds are formed.

With oxygen, indium forms three compounds, InO, In_2O_3, and In_3O_4.

In_2O_3 is formed when indium burns or its hydroxide, carbonate, nitrate, or sulfate is heated. It is a light yellow powder, easily soluble in acids unless it has been heated to a high temperature, after which it is almost insoluble. It is more infusible than Al_2O_3. InO, the sub-oxide, is formed by the careful heating of In_2O_3 with hydrogen at 300°. It is a black pyrophoric powder slowly soluble in acids. In_3O_4, isomorphous with Fe_3O_4, is formed by heating In_2O_3 above 850°.

$In(OH)_3$ is precipitated by adding the fixed alkalies to an indium salt. It is insoluble in excess of the precipitant. It has only the slightest acidic properties, only one indate being described, namely, the magnesium salt of the formula[1] $MgIn_2O_4 \cdot 3\,H_2O$. It is obtained when the chlorides of magnesium and indium are mixed and boiled.

A nitrate, $In(NO_3)_3 \cdot 4\frac{1}{2}\,H_2O$, is formed when the metal is dissolved in nitric acid. It crystallizes from nitric acid readily, but not easily from a neutral solution. It forms a double ammonium indium nitrate. If the solution of the simple nitrate is heated, a difficultly soluble basic salt is formed.

Halogen compounds, InX, InX_2, and InX_3, are all known except the mono- and di-fluorides; the oxy-chloride and -bromide, InOX, are also easily made.

$InCl_3$ is prepared by the action of an excess of chlorine on the metal, the lower chlorides, or a heated mixture of In_2O_3 and carbon. It is a white, deliquescent solid, easily soluble in water, in which it is slightly hydrolyzed. It forms double chlorides with the alkali chlorides. The solid vaporizes at 600°.

$InCl_2$ is formed by heating the metal in dry hydrogen chloride. Water

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[1] Renz, *Ber.* **34** 2763 (1901).

decomposes it, forming $InCl_3$ and In. InCl is formed by heating a mixture of $InCl_2$ and In. It is a dark red compound, which is decomposed by water, giving $InCl_3$ and In.

Sulfur forms three binary compounds with indium, In_2S, InS, and In_2S_3. The latter is prepared by direct union of the elements, by heating In_2O_3 with sulfur or H_2S; or by passing H_2S into the weakly acid solution of an indium salt. The precipitated form is yellow, and the salt formed by dry methods varies from yellow to brown. It is soluble in mineral acids, readily forms colloidal solutions, and gives complex salts with the alkali sulfides, such as $K_2In_2S_4$.

$In_2(SO_4)_3$ is a white solid, very hygroscopic and very readily soluble in water. The simple sulfate forms a hydrate with difficulty, but the ammonium, rubidium, and caesium alums crystallize readily; double sulfates resembling the alums but of the composition $M_2SO_4 \cdot In_2(SO_4)_3 \cdot 8\,H_2O$ have also been prepared with sodium, potassium, ammonium, and thallium.

Detection and Estimation. — Indium salts produce a blue-violet color in the flame,[1] in which two brilliant blue lines are visible, λ 4511.5 and λ 4102. Very small amounts of indium may be detected by microchemical methods, using rubidium indium chloride. Other reactions are: —

Precipitation of yellow In_2S_3 by H_2S from neutral or faintly acid solutions.

Precipitation of $In(OH)_3$ by alkalies or $BaCO_3$.

Precipitation of $In(CN)_3$ by KCN, soluble in excess, but hydrolyzed on standing or boiling, precipitating $In(OH)_3$.

For the estimation of indium, it may be precipitated by ammonia, the excess removed by boiling, and the precipitate dried and ignited to In_2O_3.

THALLIUM

Historical. — In March, 1861, Crookes was examining some selenium residues from a sulfuric acid factory in the Hartz Mountains. He expected to find tellurium, but being unsuccessful with chemical means, he tried the spectroscope, the use of which had in the year previous resulted in the discovery of rubidium and caesium. He found a single bright green line, which he later proved to be evidence of the presence of a new element for which he suggested the name thallium, meaning a green twig. He was unfortunate in having only a small amount of material to work with, so he did not succeed at first in correctly establishing the relationship of the element. But by May, 1862, he had collected a few grains of the metal in powder form.

Over a year after Crookes' original discovery Lamy, in France, made a similar investigation of the lead chamber deposits of a sulfuric acid plant which used a Belgian pyrite. He found thallium in considerable quantities, and by May, 1862, he had a considerable amount of the metal in lump form. He studied the physical and chemical properties of the element and many of its compounds.

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[1] For the arc spectrum of indium, see Uhler and Tauch, *Astrophys. J.* **55** 291 (1922).

The relationship of thallium to the other elements presented many puzzling problems on account of its varied resemblance to lead, silver, potassium, aluminum, and mercury. So paradoxical did the element appear to be that Dumas characterized it as the ornithorhynchus of the metals. But when Mendeléeff published his table, he argued convincingly that thallium should be placed in Group III under indium and between mercury and lead. It has always remained in this position.

Thallium is an isotope of actinium D and thorium D, and it may bear a relationship to the radioactive elements somewhat similar to that shown by lead. Soddy suggested[1] that thallium was one of the two end products of thorium disintegration, since the thorium minerals often contained too little lead to conform to the theory that lead was the only final product. Examination of thorianite, however, shows[2] that it contains less than 0.005 per cent of thallium, consequently Soddy has withdrawn the suggestion.

Occurrence. Thallium is found in considerable amounts in at least four rare minerals: crookesite, $((CuTlAg)_2Se$, contains 16–19 per cent thallium, found in a copper mine in Sweden; lorandite, $TlAsS_2$, contains 59–60 per cent thallium, found in Macedonia; vrbaite, $TlAsS_2SbS_3$, contains 29–30 per cent thallium, found in Macedonia; hutchinsonite, $(Tl, Ag, Cu)_2S \cdot As_2S_3 + PbS \cdot As_2S_3$, contains 18–25 per cent thallium.

In addition to these distinctively thallium minerals, this element is found in small quantities in a wide range of rock and minerals, showing the variety of its chemical relatives. Among these may be mentioned lepidolite, sylvine, carnallite, alunite, sphalerite, pyrite, haematite, marcasite, braunite, berzelianite, and chalcopyrite. It has also been found in mineral waters and rather widely distributed among plants. Because of its occurrence in so many minerals it is sometimes found in commercial products, such as zinc, cadmium, platinum, bismuth, tellurium, sulfuric acid, and even hydrochloric acid. The most fertile sources are the flue dusts of iron furnaces and sulfuric acid plants using thalliferous ores. Some flue dusts contain as much as 8 per cent thallium, but usually the amount is less than 0.25 per cent.

Extraction. — Crookes' method of extracting thallium from minerals was to grind the ore to a fine powder, dissolve it in aqua regia, add sulfuric acid, and evaporate to expel excess acid. Dilute to large volume, neutralize with Na_2CO_3, and add KCN to precipitate lead and bismuth. Filter and add

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[1] *Nature*, **99** 244 (1917).

[2] Cotter, *Nature*, **102** 423 (1919).

H_2S to precipitate Tl, Cd, and Hg. Dissolve the Tl_2S_3 in very dilute H_2SO_4, in which the sulfides of cadmium and mercury are insoluble.

In flue dusts, thallium is usually present as oxide or sulfate, both of which are soluble in water. The dust is thoroughly extracted with water, the solution concentrated, and TlCl precipitated by adding HCl. The extraction is sometimes made with water, slightly acidified with H_2SO_4.

The precipitation may be made with zinc, producing metallic thallium, or as sulfide or iodide.

To purify the crude thallium material it is transformed into the sulfate and its dilute solution is acidified; then H_2S is added to precipitate mercury, copper, silver, arsenic, antimony, and bismuth. Ammonia is added to remove iron and aluminium. The purified thallous sulfate is then evaporated to crystallization.

Metallurgy. — Thallium is very easily prepared from its compounds in several ways: (1) fusion of the thallous chloride or iodide with Na_2CO_3 and KCN; (2) electrolysis of the carbonate or sulfate; (3) addition of zinc to a thallous solution; (4) heating thallous oxalate in a covered crucible.

Properties. — Thallium is a white metal with blue tint, and when freshly cut it has a brilliant metallic luster. It is so soft that it may easily be marked with the thumb nail and leaves a black streak on paper. It is malleable but has little tenacity, and when an attempt is made to cut it with a file or saw it stops up the teeth of the tool. It has a crystalline structure and emits a sound similar to the tin cry. It exists in two modifications, the transition temperature being 226°. It melts at 303°, commences to volatilize at 174°, boils under atmospheric pressure at 1515°, and may be distilled in a stream of hydrogen. The coefficient of expansion is 0.000031 and the coefficient of compressibility is 2.33×10^{-6} per atmosphere. The latent heat of fusion is 7.2 calories per gram, the mean specific heat is about 0.03. The electrical conductivity[1] in reciprocal ohms per cubic centimeter at 20° is 5.28 and the magnetic susceptibility is -29×10^{-6} C.g.s. units per unit volume. In the electromotive series thallium comes between iron and cobalt.

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[1] For the potential of thallium electrodes, see *Proc. Am. Acad. Arts and Sci.* **56** 199 (1921)

Thallium oxidizes slowly and superficially in the air at ordinary temperatures, but above 100° the reaction becomes more rapid, forming thallous oxide at the lower temperatures and thallic oxide at red heat. Thallium does not react with oxygen-free water at ordinary temperatures, so one of the best methods of preserving the metal is under water which has been deprived of its air. At red heat thallium decomposes water. It combines directly with the halogens, sulfur, selenium, tellurium, phosphorus, arsenic, and antimony, but it does not unite with hydrogen, carbon, silicon, or boron. It dissolves slowly in HCl, more rapidly in H_2SO_4, and readily in HNO_3, liberating hydrogen in each case except HNO_3 and concentrated H_2SO_4.

Thallium alloys readily with many metals, especially sodium, potassium, mercury, magnesium, calcium, gold, silver, cadmium, copper, and zinc.

Uses. — Thallium compounds possess unusually high refracting power, so they are used in the manufacture of certain kinds of optical glass in which a high refractive index is desired.

A liquid amalgam containing 8.5 per cent of thallium is used in thermometers for temperatures as low as − 60°. Thallous chloride is one of the few lower chlorides which is more stable than the compound of the higher state of oxidation. So it is used as a "getter" in tungsten lamps to prolong the life of the filament.[1]

Alloys of lead and thallium [2] are distinctive in that they have higher melting points than either component. The amount of thallium varies from 3 to 65 per cent. The alloy containing 10% thallium, 20% tin, and 70% lead is resistant to the corrosive action of mixtures of sulfuric, nitric, and hydrochloric acids. This alloy is especially recommended for use as anode for the electrolytic deposition of copper, in which its corrosion is less than one-fifth that of lead alone.

Thallous chloride is changed [3] by sunlight from white through various shades to brownish black; the change is hindered by mineral acids and hastened by ammonia, ethylamine, glycerol, toluene, etc. Thallous iodide changes from yellow to green in the sunlight. These changes may become useful in photography.

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[1] *Chem. and Met.* **23** 471 (1920); *L'Industrie Elect.* **29** 472 (1920).

[2] Fink and Eldridge, *Trans. Am. Electrochem. Soc.* **40** 51 (1921); also *U. S. Pat.* 1, 384, 056, July 12, 1921.

[3] Carl Renz, *Helvetica Chem. Acta* **2** 704 (1919) and **4** 950 (1921).

Mixtures of thallous nitrate with silver, mercurous, and mercuric nitrates have low melting points and densities ranging from 4.8 to 5.3. Such mixtures are useful for separating minerals of different densities.

The " Thalofide " cell[1] is more sensitive to light, especially that of low intensity and long wave lengths than the selenium cell. Its electric resistance drops 50 per cent on exposure to a quarter foot candle. The sensitive material contains thallium, oxygen, and sulfur and is essentially an oxysulfide of thallium.

Compounds. — The compounds of thallium form two distinct classes: (*a*) thallous with a valence of 1, resembling the analogous compounds of the alkali metals in the soluble compounds, and those of lead in the more difficultly soluble ones; (*b*) thallic with valence of 3, resembling the compounds of iron and aluminium. The former may be vaporized without decomposition and are highly ionized in solution. The thallic compounds are considerably hydrolyzed and are stable only in the presence of an excess of acid. Thallous compounds are oxidized almost completely to thallic by such oxidizing agents as permanganate, chlorine, or bromine. The reduction of thallic to thallous is easily accomplished by $SnCl_2$, H_2SO_3, or metallic thallium. The addition of $(NH_4)_2S$ to a thallic salt precipitates thallous sulfide and sulfur; while KI precipitates TlI and I. The contrasting character of the thallous and thallic salts is shown by the fact that they readily form complex salts with each other, such as $TlCl_3 \cdot 3\,TlCl$. A thallous-thallic alum, $Tl\,Tl(SO_4)_2 \cdot 12\,H_2O$, is described, but the existence of such molecules is open to question because of the difficulty of obtaining a definite crystalline form. It seems certain, however, that both the thallous and thallic conditions are present in solution.

Thallium compounds are cumulative poisons, resembling lead.

Thallous Salts. — The *oxide*, Tl_2O, is a heavy black powder, which is formed when the metal is oxidized at low temperatures, or when Tl(OH) is heated at 100°. It absorbs water readily, producing the hydroxide, and at 300° it melts to a liquid which attacks glass rapidly. It is easily reduced or oxidized.

The *hydroxide*, Tl(OH), forms yellow crystalline needles, and may be formed by dissolving thallous oxide in water or by adding baryta to thallous

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[1] Case, *Phys. Rev.* (2) **15** 289 (1920) and *U. S. Pats.* 1301 227 (1919) and 1316 350 (1919)

sulfate. It is readily soluble in both water and alcohol, its solutions are strongly alkaline, absorbing carbon dioxide greedily and attacking glass and porcelain. On heating it gives the oxide, and with ozone, hydrogen peroxide, and other oxidizing agents it produces thallic hydroxide.

The *halide compounds* are all easily prepared by direct union of the elements or the action of the halogen acid upon the oxide, hydroxide, or carbonate. The chloride, bromide, and iodide are insoluble in cold water, soluble in hot water, and are made by precipitation. They resemble the lead salts closely in appearance and general properties. Several double halides have been prepared.[1]

The *nitrate*, $TlNO_3$, forms anhydrous crystals which are insoluble in alcohol and soluble in water to the extent of 9.55 grams in 100 grams of water at 20°. The crystals begin to decompose at 300°, and at 450° the decomposition is rapid, although a little of the salt sublimes without decomposition.

The *sulfide*,[2] Tl_2S, is obtained by adding H_2S or $(NH_4)_2S$ to an alkaline or faintly acid thallous solution. It is bluish black, generally crystalline, insoluble in ammonium sulfide. On exposure to air it is oxidized to the sulfate.

The *sulfate*, Tl_2SO_4, is isomorphous with potassium sulfate, melts at 632°, and volatilizes without decomposition above red heat. 100 grams of water dissolve 4.87 grams of salt at 20°. It readily forms alums with the trivalent sulfates and takes the place of the alkali sulfates in such double salts as $R'_2SO_4 \cdot R''SO_4 \cdot 6H_2O$, in which R' represents an alkali metal or thallium and R'' represents magnesium, zinc, iron, nickel, cobalt, copper, manganese, and cadmium. The double sulfates, $Tl_2SO_4 \cdot Tl_2(SO_4)_3$ and $5Tl_2SO_4 \cdot Tl_2(SO_4)_3$, have been shown to exist, the former above 48° and the latter between 23°.5 and 30°. At other temperatures only mixtures of these salts can exist.[3]

Other thallous salts are the soluble carbonate, chlorate, perchlorate, ferrocyanide[4] and the nitrites[5] and the sparingly soluble chloroplatinate, cobaltinitrite, chromate,[6] and double hyposulfites.

Thallic Salts. The *oxide*, Tl_2O_3, is produced by oxidation of the metal at elevated temperatures or by heating $Tl(OH)_3$; by adding H_2O_2 to a cold alkaline solution of a thallous salt; anodic oxidation during the electrolysis at low potential of a neutral solution of thallous sulfate or nitrate. It is brown, may be crystalline, insoluble in water and alkalies, decomposes above 800°, yielding thallous oxide and oxygen.

The *hydroxide*, $Tl(OH)_3$, or better $TlO \cdot OH$, is prepared by adding the alkali hydroxides or ammonia to a thallic solution. If $Tl(OH)_3$ exists, it is changed to $TlO \cdot OH$ on heating or drying; the dehydration to Tl_2O_3 is complete at 110°–120°. When freshly prepared it is readily soluble in

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[1] Canneri and Perina, *Gazz. chim. ital.* **52** I 231 (1922); C. A. **16** 2046 (1922).

[2] See H. Pélabon, *Compt. rend.* **173** 142 (1921).

[3] Berroth and Esperschied, *Z. anorg. allgem. chem.* **121** 361 (1922).

[4] Cuttica and Paciello, *Gazz. chim. ital.* **51** I 160 (1921); C. A. **15** 3037 (1921).

[5] *Ibid.* **52** I 141 (1922); C. A. **16** 2086 (1922).

[6] G. Canneri, *Gazz. chim. ital.* **52** I 33 (1922); C. A. **16** 1715 (1922).

acids, but after drying it dissolves slowly. It is a brown, amorphous substance, resembling $Fe(OH)_3$ in appearance, and extremely insoluble in water, having a solubility product at 25° of 10^{-53}.

The *chloride*, $TlCl_3 \cdot H_2O$, is made by passing chlorine into water in which TlCl is suspended, and allowing the saturated solution to stand. A tetrahydrate is also formed, from which the anhydrous salt is prepared by dehydrating at ordinary temperatures. With a small amount of water thallic chloride forms a clear solution, but on dilution the salt suffers hydrolysis.

The *bromide and iodide* are similar to the chloride but still less stable. The iodide behaves as though it were a mixture of thallic iodide TlI_3 and thallous periodide $TlI \cdot I_2$ analogous to $KI \cdot I_2$. It has been suggested that it is a tautomeric compound,[1] sometimes thallous and at other times thallic in behavior. It readily forms double salts.

The *nitrate*, $Tl(NO_3)_3$, is prepared by dissolving Tl_2O_3 in nitric acid. It forms deliquescent crystals, $Tl(NO_3)_3 \cdot 3\,H_2O$, is easily hydrolyzed and decomposed, and forms double nitrates.

The *sulfide*, Tl_2S_3, is made by direct union of the elements. Attempt to prepare it by precipitation give Tl_2S and S. It is a black solid, brittle below 12°, soft and plastic at higher temperatures.

The *sulfate*, $Tl_2(SO_4)_3$, is easily hydrolyzed by water, producing a basic salt. It forms double compounds very similar to the alums, such as $(NH_4)_2SO_4 \cdot Tl_2(SO_4)_3 \cdot 8\,H_2O$, but the formation of true alums is still doubtful.

Detection and Estimation. — All thallium compounds impart a green color to the flame and yield a green line at λ 5350.

Qualitative tests for thallous compounds are: (1) brown precipitate Tl_2S with H_2S or $(NH_4)_2S$ in neutral or slightly acid solutions; no precipitate in presence of a strong acid; (2) soluble halides produce TlCl, white, TlBr, pale yellow or TlI, bright yellow; (3) K_2CrO_4 precipitates yellow, Tl_2CrO_4; (4) H_2PtCl_6 precipitates yellow, Tl_2PtCl_6 (quantitative); (5) sodium cobaltinitrite precipitates thallous salts quantitatively as thallous cobaltinitrite, brilliant red.

Thallic salts are identified by the brown precipitate produced by ammonia or the alkali hydroxides; or by reduction to the thallous state and the tests given above.

Quantitatively, thallium is determined as the iodide, chloroplatinate, chromate, or sulfate. Thallium may be determined volumetrically, also, by the use of permanganate [2] or iodometric measurement.

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[1] Abegg and Maitland, *Zeit. anorg. Chem.* **49** 341 (1906).

[2] A. J. Berry, *J. Chem. Soc.* **121** 394 (1922).

CHAPTER VIII

GROUP IV — TITANIUM

THE elements which comprise Group IV occupy the exact center of the periodic table. Recalling that each series of the table shows a gradual transition from metal to non-metal, it is to be expected that the elements falling in the center of the series will be distinctly amphoteric and electrochemically indifferent. There ought also to be less marked differences between the members of Divisions A and B than in the other groups of the table. So slight are these differences in fact that the division into sub-groups is scarcely necessary except for convenience. It is to be noted, however, that the differences between A and B sub-groups increase as we pass from Group IV toward either end of the table.

All the members of this group are metallic in nature except the first two members, which are mainly acidic. All the metallic elements except tin and lead have high melting points; none suffer more than superficial oxidation at low temperatures; but all the elements of the group, when heated strongly, combine readily with oxygen, yielding the dioxide, except in the case of lead. The dioxides of the elements of lower atomic weights are acidic, but the basicity increases with increased atomic weight of the element.

The principal valence of Group IV elements is 4, each element of the group except lead forming its principal series of compounds in the quadrivalent state. Valences of 2 are common, and 3 occasional. The quadrivalent halogen compounds of most of the elements form characteristic double derivatives with the alkali halides, of the type $M^{I}_{2}M^{IV}X_{6}$. These compounds, especially the fluorides, are of much importance.

Nowhere does the unique character of the first member of the family stand out more strikingly than with carbon in Group IV. The ability of carbon atoms to form countless chain and ring compounds, the relationship of carbon to all forms of life, and its peculiar chemical behavior make this element stand in a class by itself. It may be taken for convenience as an intro-ductory element for Group IV, but it is certainly not "typical" of either subgroup A or B. The element silicon resemble carbon in some particulars, consequently it is customary to consider both these ele-ments as introductory to the subgroups. The usual arrangement is shown in Fig. 10. The A division includes titanium, zirconiu cerium, thorium, and the B division germa-nium, tin, and lead. The blanks betwee cerium and thorium and between tin an lead indicate marked differences in prop-erties between these pairs of elements rather than spaces which may be filled b undiscovered elements.

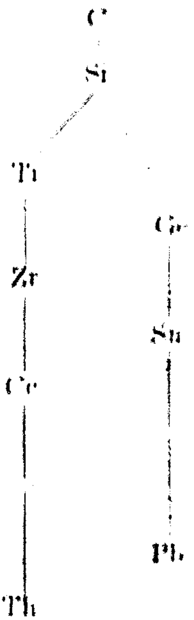

Fig. 10

The members of subgroup A are more less basic than the rare earth elements which they resemble in many respects This decreased basicity is shown not onl by the amphoteric oxides and the hydrol-ysis of the salts, but also by the greate tendency to form complex salts. Titaniur resembles silicon, especially in many of th native minerals in which TiO_2 and SiO replace each other freely, and also in the isomorphism of th titanates and silicates. The greater basicity of titanium an the succeeding elements is shown by the decreasing hydrolysi of their quadrivalent salts as the atomic weight of th metal increases. Titanium hydroxide dissolves in alkalie forming titanates; zirconium hydroxide does not dissolv in alkalies, though zirconates may be prepared by dry methods cerium and thorium hydroxides are basic only.

None of the elements of the A sub-group form definite hy-droxides of the formula $M(OH)_4$. Attempts to precipitat $Ce(OH)_4$ yield a mixture of this compound and a basic salt while the other three elements form hydrated oxides which los water continuously and show no definite compounds until th dehydration is complete. The hydroxides all readily form col-loidal solutions.

The members of the A division form superoxides which ar precipitated by the alkalies in the presence of hydrogen peroxide. This behavior is sharply in contrast with the elements of the B division, and is intimately related to the greater electropositiveness of the A sub-group. The physical constants of sub-group A are shown in Table XXIV.

TABLE XXIV

Properties of Titanium Sub-Group

	TITANIUM	ZIRCONIUM	CERIUM	THORIUM
Atomic Weight . .	48.1	90.6	140.25	232.15
Specific Gravity . .	4.87	4.25	6.73	11.00
Atomic Volume . .	9.88	21.32	19.92	21.13
Melting Point . .	1795°	1500°	635°	1450°

TITANIUM[1]

Historical. — Rev. William Gregor in 1789 discovered a new metal in the magnetic sand from Menachan, Cornwall, which was known as menachanite or more commonly now as ilmenite. He suggested the name menachin for the new element. A few years later, Klaproth found a new element in rutile, and suggested the name titanium, from the Titans, the giants of Grecian mythology. In 1797, he proved that menachin and titanium were identical and the former name was dropped. The pure oxide was not prepared until 1821, when Rose successfully purified TiO_2. Early attempts were made to produce the element by reduction of the oxide with carbon. Berzelius in 1825 prepared a metallic substance which was supposed to be the element until in 1849 Wöhler proved it to be a cyanonitride.

Occurrence. — Titanium is usually regarded as a rare element, but it is one of the 10 more abundant elements in the earth's crust, TiO_2 making up 0.73 per cent of the whole lithosphere. It is almost twice as abundant as carbon and exceeds chlorine, phosphorus, and sulfur in abundance. It resembles silicon in its combinations, since it is never found in the free state, but in combination with oxygen either as the simple oxide or as titanates.

As TiO_2 it occurs in three distinct crystalline forms known as rutile, brookite, and anatase, the first named being common

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[1] See report by R. J. Anderson, U. S. Bur. of Mines, Serial No. 2406 (1922).

and the two last rare minerals. The relative abundance of the three forms is shown by their cost. During the latter part of 1920 imported rutile sold wholesale at 12-15 cents per pound; in March, 1921, brookite was quoted at $10 per pound, and anatase at $230 per pound. Rutile forms in tetragonal crystals with the relations of the axes $a : h = 1 : 0.6442$. Its hardness varies from 6 to 6.5, and specific gravity from 4.18 to 4.25. Anatase, called sometimes octahedrite, also belongs to the tetragonal system, but its crystals have the ratio $a : h = 1 : 1.777$; its hardness is 5.5 to 6, and specific gravity 3.82 – 3.95. Brookite forms orthorhombic crystals which are usually flat prisms. The three crystalline forms differ materially in refractive power and other physical properties, and furnish one of the best examples known of a trimorphous body. It is isotrimorphous with stannic oxide.

In addition to the simple oxide, titanium occurs as ilmenite,[1] $FeTiO_3$, and titaniferous magnetite, titanite, $CaO \cdot TiO_2 \cdot SiO_2$, and other titanates of calcium, iron, aluminum, etc.; also in silicates, columbates, and tantalates. It is found in smaller proportions in many iron ores, such as titaniferous magnetite, from which it finds its way into iron products; in basalt, mica, sand, gravel, clay, soils, and mineral waters. Certain complex monazites and certain bauxites are possible commercial sources of titanium. F. W. Clarke says[2] that out of 800 igneous rocks analyzed at the U. S. Geological Survey laboratory, 784 contained the element titanium. From these sources it finds its way into the ashes of all plants, and the flesh and bone of all animals. It has been found in the meteorites, the sun, and many of the stars.

The commercial sources of titanium are rutile and ilmenite. The former is found in granite gneiss, slate, quartz, or feldspar, in many localities relatively few of which have produced commercial quantities. The chief commercial sources are Norway, northern Quebec, South Australia, and Virginia. The Virginia rutile is in two distinct regions, although Nelson County has so far produced all the commercial material. The belt of rutile-bearing rock is 16 miles long and has a maximum width not exceeding 2½ miles.

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[1] Ilmenites vary in composition from the pure iron titanate through $(FeTi)_2O_3$ to Fe_2O_3.

[2] *Bull.* 616, U. S. Geological Survey, p. 21.

Ilmenite and titaniferous magnetite are found in many localities, the best known foreign deposits being at St. Urbain, Quebec, and in Norway and Sweden. In the United States[1] two deposits are notable: at Lake Sanford, New York, the ore averages 62.8 per cent magnetite and 30 per cent ilmenite; at Iron Mountain, Wyoming, the average composition corresponds to 49.8 per cent magnetite and 40.15 per cent ilmenite. The two deposits are estimated to contain many millions of tons of ore. A recently developed deposit at Pablo Beach, Florida, was producing in 1919 considerable quantities of ilmenite and rutile, along with zircon and monazite.

The production of titanium ores fluctuates widely from year to year. About 200 short tons of rutile (95% TiO_2) are marketed annually in the United States. The amount of ilmenite produced was 1644 tons in 1918, but in 1920 only 268 tons were reported. A small amount of rutile is imported from Norway, and considerable ferro-carbon titanium is exported. The 1922 prices are about as follows: rutile (95%), 12 cents per pound; ilmenite (52% TiO_2), 15 cents per pound; ferro-carbon titanium (15–18%), 20 cents per pound; and carbon-free titanium, 30 cents per pound of contained titanium.

Extraction. — Rutile is exceedingly resistant to chemical action. Either rutile or ilmenite may be brought into solution by fusion with alkali, alkali carbonate, or bisulfate and extracting with acid. By adding ammonia to this solution a mixture of iron and titanium oxides is thrown down. Another satisfactory method fuses the ore with carbon in an electric furnace, subjects the carbides to the action of chlorine, and distills off the volatile titanium tetrachloride.[2]

Iron and titanium may be separated by several methods: (1) dissolving the mixed oxides in HCl and extracting $FeCl_3$ with ether;[3] (2) reducing the iron with $NaHSO_3$, adding KCN and ammonia and heating nearly to boiling, TiO_2 precipitates, iron remains in solution as ferrocyanide;[4] (3) adding ammonium tartrate to hold the titanium in solution then precipitating iron with ammonium sulfide, evaporating the filtrate with a mixture of sulfuric and nitric acids to destroy the tartaric acid and pre-

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[1] See *Bull.* 64, U. S. Bureau of Mines.

[2] Stähler, *Ber.* **37** 4405 (1904); *ibid.* **38** 2619 (1905).

[3] Barneby and Isham, *Jour. Am. Chem. Soc.* **32** 957 (1910)

[4] Bornemann and Schirmeister, *Metallurgie,* 7 723 (1910).

cipitating the titanium with ammonia;[1] (4) heating a mixture of ferric and titanium oxides in the presence of HCl and S_2Cl_2; the iron distills out, leaving TiO_2 unattacked.[2]

Metallurgy. — Titanium is obtained in the metallic condition with the greatest difficulty, because of its extremely high melting point, the ease with which it unites with oxygen and nitrogen of the air, or hydrogen and carbon as reducing agents, and its readiness to alloy with most of the common metals which might be used for utensils or electrodes.

The methods which have been used to prepare the element are as follows: (1) reduction of potassium titanofluoride with sodium or potassium — this method does not effect complete reduction; (2) reduction of $TiCl_4$ with hydrogen is not successful, but heating the tetrachloride with sodium in a cast iron bomb gave[3] a product containing 95–99.7% titanium; (3) reduction of TiO_2 with magnesium, silicon, or aluminium does not give good results because titanium alloys with these metals; (4) reduction of TiO_2 with carbon gave good results[4] if the temperature was high enough to decompose the compounds formed between titanium and carbon and nitrogen. In this way carbon is the only impurity, and it may partly be removed by fusion with more TiO_2. Moissan obtained in this way a product which contained 98 per cent titanium; (5) reduction[5] of TiO_2 by calcium shavings in an evacuated iron dish. The product was very pure; (6) electrolysis of a solution of TiO_2 in fused $CaCl_2$ gave[6] a product nearly free from nitrogen and carbon.

These methods all gave the element in powder form. The fused metal was prepared[7] by pressing the powder into bars at 70,000 atmospheres pressure and using these as electrodes in a vacuum arc. The metal fused in the form of globules on the ends of the electrodes.

It is worthy of note that the metallurgy of the element titanium is in the same state of development at the present time that aluminium was forty years ago.

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[1] Thornton, *Am. Jour. Sci.* **34** (iv) 214 (1912).

[2] Bourion, *Compt. rend.* **154** 1229 (1912).

[3] Nilson and Pettersson, *Zeit. Phys. Chem.* **1** 28 (1887); *Zeit. anorg. Chem.* **99** 123 (1917); and *Trans. Am. Electrochem. Soc.* **37** 513 (1920).

[4] Moissan, *Compt. rend.* **120** 290 (1895).

[5] Wedekind, *Annalen*, **395** 149 (1913).

[6] Borchers and Huppertz, *Metallurgie*, vol. 1, p. 362 (1904).

[7] Weiss and Kayser, *Zeit. anorg. Chem.* **65** 388 (1910).

Properties. In the amorphous form, titanium is a dark gray powder closely resembling reduced iron in appearance. It is paramagnetic. The fused metal resembles polished steel and is sufficiently hard to scratch quartz; when cold it is so brittle that it may be powdered in an agate mortar, but when properly prepared it may be worked easily,[1] at red heat it may be forged and drawn, although it possesses little ductility. The fractured surface has a brilliant luster, sometimes with a tint of yellow somewhat resembling bronze. When rubbed against steel it gives bright sparks. The specific heat rises rapidly with increase of temperature, being 0.1125 between 0° and 100° and 0.162 between 0° and 440°; consequently the atomic heat varies from 5.4 to 7.77 for the same intervals. In the crystalline form it is isomorphous with zirconium and silicon.

Titanium is stable in the air, almost no oxidation taking place up to 120° C. But when heated to 610° in oxygen the metal takes fire and burns with dazzling brilliancy, producing TiO_2. The heat of combustion is 24,432 calories per equivalent. At 800° it begins to burn in nitrogen, also forming the nitride TiN. This is the only element known which burns vigorously in nitrogen. When heated in the air a mixture of oxide and nitride results. When titanium dioxide is heated in air in the presence of carbon a compound called cyanonitride of uncertain composition is formed. It is accordingly found in blast furnaces which use titaniferous ores. It forms brilliant red cubes, extremely hard and resistant to acids, but like the nitride it yields ammonia when heated with steam. Hence, both these compounds have been proposed for the fixation of atmospheric nitrogen. At 700°–800° titanium decomposes steam. When mixed with red lead and heated, the element is oxidized so rapidly that it is thrown out of the crucible with loud detonations.

Titanium burns in chlorine at 350°, and with bromine or iodine at somewhat higher temperatures, forming salts of the type TiX_4. When heated, it combines directly with almost all non-metals, even with carbon, silicon, and boron at the temperature of the electric furnace. The borides and silicides are as hard as diamonds. At low temperatures the element resists the action of acids, but it dissolves readily on warming.

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[1] R. J. Anderson, *Jour. Frank. Inst.* **184** 467 (1917).

Hot dilute HCl and dilute H_2SO_4 yield hydrogen and a trivalent salt; dilute nitric acid oxidizes it, giving titanic acid, while concentrated nitric acid, especially when hot, yields the difficultly soluble metatitanic acid; hydrofluoric acid dissolves it very readily and even acetic acid attacks it slowly.

It alloys with most of the metals, especially copper, tin, iron, aluminium, chromium, cobalt, molybdenum, and tungsten.

Uses. The principal uses for titanium are in connection with its alloys, of which by far the most important is ferrotitanium. Until very recently iron ores containing more than 1 per cent of titanium were not used because of the difficulties encountered when attempts were made to smelt in the blast furnace. A pasty slag was produced, titanium nitride and cyanonitride formed deposits, the furnace was choked up, the lining was attacked, and the fuel consumption was high. As a result of these experiences blast furnace operators are still generally prejudiced against the use of titaniferous ores. Principally through the skillful researches of A. J. Rossi the problem[1] has been solved, and for over 25 years iron ores containing up to 15–20 per cent TiO_2 have been smelted, yielding a fusible slag and a superior grade of pig iron low in both sulfur and phosphorus. Greatest success in this direction has come, however, in the use of the electric furnace, because of the higher temperatures easily available.

Ferrotitanium is produced in two grades — (1) that containing considerable carbon is called ferro-carbon titanium. It is produced by the reduction of ilmenite with coke or of rutile with carbon in a bath of liquid iron or steel; an electric furnace giving a temperature of at least 1900° C. is required. The product contains 15–18% titanium, 5–8% carbon, about 1.5% silicon, and other impurities in small amounts. The carbon content may be reduced by remelting with TiO_2 or aluminium.[2] (2) Carbon-free ferrotitanium is produced by reduction with aluminium. In Germany a modified Goldschmidt thermit reduction is used which adds BaO_2 or Na_2O_2 to accelerate the

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[1] See Rossi, *Jour. Am. Chem. Soc.* **12** 90 (1890) and *Trans. Am. Inst. Min. Eng.* **21** 832 (1893); Von Maltitz, *Stahl und Eisen*, **29** 1503 (1909); *Bull.* 64, U. S. Bur. of Mines; also Perkin Medal addresses for 1917, *Jour. Ind. and Eng. Chem.* **10** 138 (1918); W. M. Goodwin, *Trans. Roy. Can. Inst.* **13** 35 (1921); G. F. Comstock, *Chem. and Met.* **26** 105 (1922); *Iron Age*, **108** 1067 (1921) and **109** 97 (1922).

[2] *U. S. Pats.* 1,374,035 and 1,374,036, April 5, 1921.

reaction; in America the Rossi process[1] is used, in which an electric furnace produces a bath of molten aluminium. To this is added the desired amount of scrap iron, or high-grade iron ore if a very low-carbon product is essential. After a layer of molten iron is formed below the aluminium, the titanium material is added, either in the form of titaniferous iron ore or rutile or even titanium slag. The reaction is exothermic so little current is required to maintain the reaction temperature. This process yields an alloy containing up to 75 per cent titanium and with from 0.12 to 0.8 per cent carbon. The American product usually contains about 25% titanium, 5% aluminium, and 1 to 1.5% silicon. This gives a low-melting titanium aluminate on fusion in the steel bath. There is keen rivalry between the two methods of producing the ferro alloy.[2]

The use of ferro-titanium in the steel industry is rapidly gaining favor, especially in the United States. The effect of the titanium is twofold: (1) its striking affinity for both oxygen and nitrogen makes it efficient for the removal of the last traces of these elements; (2) it apparently has the unique property of causing the separation of occluded substances like oxides and sulfides of iron and manganese, silica, slag, etc. As ordinarily used, very little, if any, of the titanium remains in the steel, hence its purpose is purely that of a cleansing agent. The fluidity of the slag is increased because of the exothermic reactions which accompany the removal of the impurities, hence the separation of the slag is more nearly complete. The importance of removing oxygen, nitrogen, and iron oxides is becoming more and more evident, as experiments tend to show that these impurities are more troublesome than small amounts of sulfur.[3]

The beneficial effect of titanium treatment is most evident in Bessemer steel; it is less marked in open-hearth steel and it is even applied to crucible and electric steels and cast iron. The addition of titanium is best accomplished as an iron alloy. If the element is added alone, its high melting point and low specific gravity make it difficult to obtain a good mix. In

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[1] Auguste J. Rossi, *Elect. Chem. Ind.* **1** 523 (1903).

[2] See R. J. Anderson, *Jour. Frank. Inst.* **184** 467 (1917); C. V. Slocum, *Trans. Am. Electrochem. Soc.* **20** 265 (1911).

[3] See *Iron Age*, Jan. 13, 1916, p. 146; *Bull. A. I. M. E.*, Oct. 1916, p. 1841; *Chem. and Met.* **11** 144 (1913).

American practice the ferrotitanium is added to the ladle after the other cleansing agents and as the charge is drawn. To give time for the purification the ladle is held 5-10 minutes, during which the internal reactions keep the mass fluid, an actual rise of temperature being common. The amount added varies from 2 to 20 pounds per ton, depending on the amount of impurities it is expected to remove and the purpose for which the steel is to be used. If larger amounts are used, some of the titanium remains in the steel, but apparently it has little effect upon the structure, since samples containing as much as 10 per cent titanium exhibit the normal pearlitic structure of straight carbon steels. Titanium in iron occurs free or as nitride or cyanamide.[1] The free element enters into solid solution in molten iron and forms iron titanide which is miscible with iron in all proportions. The hardness of the alloy increases rapidly up to 8 per cent titanium, then the hardness increases more slowly. The cost of titanium treatment varies from 25 cents to $2 per ton.

The properties claimed[2] for steel which has been treated with titanium are greater strength and greater resistance to abrasion and shock. It is said the ultimate strength may be increased 15 per cent without decreasing the elasticity. Such steels are recommended for gears, pinions, propeller shafts, driving rods, tools, and car wheels. The largest use seems to have been in steel rails, where the greater toughness and strength has increased the life of the rails as much as 200 to 400 per cent. Titanium treatment improves alloy steels also, especially those containing nickel, chromium, or manganese.

The rapid growth in popularity of the titanium steels is shown by the rate of production in the United States. The first heat of titanium steel was made in 1907, and by 1913 more tons of titanium steel were made than all other alloy steels put together. The output is as follows :—

1910 . .	326,300 tons
1911 . .	410,500 tons
1912 . .	550,000 tons
1917 . .	2,200,000 tons
1918 . .	2,400,000 tons

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[1] *Zeit. Metallkunde*, **12** (1920).

[2] *Jour. Ind. and Eng. Chem.* **2** 280 (1910); Bradley Stoughton, *Metallurgy of Iron and Steel*; see, also, W. A. Janssen, *Trans. Am. Foundrymen's Assoc.* **25** 374 (1916).

The use of titanium in cast iron has been tried,[1] but the results are somewhat less convincing. The alloy used for this purpose generally contains from 0.1 to 1.0 per cent of titanium. The effect of the titanium is to remove oxygen, nitrogen, and sulfur; to throw down graphite and to prevent the precipitation of iron carbide. It is claimed that the product has increased strength, soundness, and hardness, as well as improved machining qualities.

Treatment of iron and other metals with titanium has a considerable effect upon the magnetic properties. Iron which has been treated with titanium has higher magnetization curves and lower hysteresis losses.[2] These effects are probably produced by the cleansing action of titanium. If some titanium remains in the iron, the magnetic properties are lower than pure iron. Ferrosilicon, when treated with titanium, gives an exceedingly high permeability and low hysteresis loss.

Other alloys of titanium are prepared,[3] usually from rutile, since generally these alloys must contain little or no iron. These alloys are made in the electric furnace or by the Goldschmidt process. Cupro-titanium containing 5–12 per cent titanium is made by adding copper to the aluminium bath, then adding rutile. The addition of 1–2 per cent of this alloy to molten copper or brass produces a metal which can easily be cast in sand and is free from blowholes.[4] When present in small amounts, titanium raises the tensile strength and lowers the ductility of copper. The toughness and resiliency of aluminium is increased by 2 per cent of titanium, but this alloy lacks durability. A titanium-silver alloy [5] added to molten silver improves the structure of the metal and prevents "spitting" during the cooling process. An alloy of manganese, containing 30–35 per cent titanium, is used as a deoxidizer in bronze practice. An alloy of silicon and titanium is produced [6] by smelting TiO_2 and SiO_2 with carbon in the electric furnace. It is used for the addition of both silicon and titanium to steel.

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[1] R. Moldenke, *Trans. Am. Foundrymen's Assoc.* **17** 57 (1908); *Bull. Am. Inst. Min. Eng.* 1912, p. 1245; Sheeon, *Chem. Eng.* **13** 257 (1911); Stoughton, *Trans. Am. Inst. Min. Eng.* **44** 282 (1912).

[2] *Trans. Am. Electrochem. Soc.* **37** 513 (1920).

[3] See *Mineral Industry*, **9** 715 (1900).

[4] See *Metal und Erz.* **11** 10 and 48 (1914).

[5] Rossi, *U. S. Pats.* 1,024,476 and 1,025,426, Aug. 1912.

[6] *Jour. Soc. Chem. Ind.* **29** 636 (1910); see, also, *Iron Age*, June 1, 1918 p. 1540.

Other uses of titanium and its compounds are numerou Frequent efforts have been made[1] to utilize the material f artificial lighting media, where high efficiency is produced b the brilliant spectrum, which is one of the richest of all th elements. The high fusion and vaporization temperatur are also distinct advantages. In arc lamps in which titaniu preparations are used, the general arrangement employs th titanium in the cathode which is placed above a copper anod The light is emitted almost entirely from the arc itself, whi the color, which is a pure white, comes entirely from the tita nium pencil, the copper remaining inactive and wasting awa very slowly. The lamps require a direct current. For a lamp electrodes, the carbide, the oxide, ferrotitanium, an various mixtures have been used. The dioxide alone does no give good results because it is a poor conductor and it is difficu to start the arc. Pencils made of a "suboxide," prepare from the dioxide by heating with carbon, are somewhat mo successful, but they have a short life and the troublesome dio ide deposits at the end of the pencils. When the dioxide fused with magnetite, chromite, and potassium fluoride, a ma terial is produced which gives efficient electrodes. The arc steady, but it throws off tiny glowing particles which soo make the glass globe opaque. Pencils of titanium carbi have been most successful, but they burn away rapidly, an the arc soon becomes unsteady, due to the accumulation of th dioxide. The life of the pencil is increased by adding about 1 per cent of chromium carbide, the flickering is decreased b adding cryolite or the titanofluoride of calcium or cerium, an the tendency to throw off sparks is decreased by adding su fur or selenium. One decided advantage in the use of titaniu carbide electrodes is that the arc burns almost noiseless A hollow carbon pencil with the center filled with a titaniu mixture has also been successful. Another device used f securing the beneficial effects of titanium consists in suppl ing the incandescent arc with an atmosphere of $TiCl_4$ $TiCl_2Br_2$.[2]

For incandescent filaments, metallic titanium is remarkab efficient because of its high melting point, low conductivit

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[1] Ladoff, *Jour. Ind. and Eng. Chem.* **1** 711 (1909).

[2] *Chem. and Met. Eng.* **13** 915 (1915).

slight tendency to vaporize, and the brilliant light emitted. The filaments must be made of very pure titanium, since even traces of impurities render them extremely fragile. The cost of producing the pure metal makes these filaments prohibitive. Efforts have also been made to utilize the brilliant light of titania in incandescent gas mantles.

As mordants and dyes the compounds of titanium find a variety of important uses in dyeing cotton, wool, paper, and leather. If leather or textile goods are immersed in a solution of a titanium salt and then steamed, the hydrated dioxide is precipitated. This forms permanent lakes, producing brilliant colors when the material is put through the dye bath. In the more delicate fabrics titanium salts of organic acids are used to prevent injury by free mineral acids. Formerly quadrivalent titanium compounds were used for this purpose, but they have been very largely displaced by trivalent salts, which are serviceable not only as mordants but also because of their great power as acid-reducing agents. The chloride, $TiCl_3$, and the sulfate, $Ti_2(SO_4)_3$, are the salts generally used. In using direct dyes on cotton goods, sometimes the color is uneven or the shade too deep. If it is necessary to remove the dye, a process called stripping, it may usually be done quickly by immersion in a 1 to 5 per cent solution of titanous salt. In the same way in figured goods in which the color has " run," the background may be whitened.

Potassium titanium oxalate is used extensively for both mordanting and dyeing of leather, giving various shades from yellow to brown. The lactates of titanium under the trade name " corichrome " are used in the leather industry both as mordants and " strikers." The use of titanium salts in dyeing leather does not produce so brittle a product as iron salts.

Titanium pigments are known in several colors. The ferrocyanide has a fine green color, used in place of arsenical pigments in wall papers. Various shades of yellow, brown, and red are produced by roasting rutile or ilmenite with other materials. A light yellow pigment made from ilmenite[1] forms a protective coating for iron and steel, especially when mixed with asphalt. Precipitated TiO_2, titanium white or " titanox,"

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[1] R. J. Anderson, *Jour. Frank. Inst.* **184** 467 (1917).

has been used successfully[1] as a paint base, where its permanence, great opacity, and non-poisonous nature have increased its popularity very rapidly. It may be used in mixture with $BaSO_4$, forming essentially a titanium lithopone. Calcium titanate also gives promise of becoming a useful paint material.[2] Titanium paint is unaffected by sea water,[3] has no saponifying action on linseed oil, and has more than a third greater covering power than white lead. The manufacture of titanium paints has reached large proportions at Niagara Falls and in Norway.

Ceramic colors frequently utilize titanium compounds. Rutile is used to give a soft yellow under-glaze color to porcelain, replacing the more expensive uranium compounds for this purpose. It is also used in tinting artificial teeth, porcelain, tiles, etc., in which the amount varies from 0.5 to 5 per cent, depending on the depth of color desired. The characteristic blue color of sapphires is presumably due to trivalent titanium, since synthetic stones identical with the natural product have been prepared[4] by fusing alumina with TiO_2 and Fe_2O_3.

Titanium trichloride has been used[5] extensively in the laboratory as a powerful reducing agent. It reduces many organic substances and one part of gold in twenty million may be detected by the colloidal solution which it produces. In about 1 per cent solutions it is convenient for the quantitative determination of iron, copper,[6] tin, chromium, hydrogen peroxide, chlorates, nitrates, hydroxylamine, and many other substances.[7] Its use has been much more general in Europe than in the United States, where its introduction has been hindered by the difficulty of preserving an accurately standardized solution. Its popularity is increasing rapidly and 15–20 per cent solutions of titanous chloride or sulfate may now be obtained from

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[1] H. A. Gardner, *Circular* 62, Educ. Bur. Paint Mfg. Assn. of U. S., April 1919; also *Chem. Ztg.* **42**, 356 (1918).

[2] *U. S. Pat.* 1,436,164, Nov. 21, 1922.

[3] *Chemie et industrie*, **6** 815 (1921).

[4] Verneuil, *Compt. rend.* **150** 185 (1910).

[5] See *Ber.* **36** 166, 1549 (1903); Brandt, *Chem. Ztg.* **42** 433, 450 (1918); *Jour. Am. Chem. Soc.* **43** 91 (1921); also, *New Reduction Methods in Volumetric Analysis*, Longmans, Green and Company (1918); Hendrixson and Verbeck, *Jour. Am. Chem. Soc.* **44** 2382 (1922); Hans Rathsburg, *Ber.* **54**, B 3183 (1921).

[6] W. M. Thornton, Jr., *Jour. Am. Chem. Soc.* **44** 998 (1922).

[7] "Titration of Azo Dyes with $TiCl_3$," D. O. Jones and H. R. Lee, *Jour. Ind. and Eng. Chem.* **14** 46 (1922).

American manufacturers. These solutions may safely be diluted for use if sufficient acid is added to prevent hydrolysis. The standard solutions should be kept in an atmosphere of hydrogen, but the titration may be made in air although somewhat better results are obtained in an atmosphere of carbon dioxide.

Titanium tetrachloride came into great prominence during the war as a material for producing toxic smoke. Its value in this connection depends upon the fact that the colorless liquid is quickly hydrolyzed in moist air, forming the dense hydrate, $TiCl_4 \cdot 5\,H_2O$. If the amount of moisture is excessive, the hydrolysis is complete, giving HCl and $Ti(OH)_4$, which has less obscuring power. In case the latter reaction takes place the density of the cloud is greatly increased by adding NH_3, which forms a cloud of NH_4Cl. If, however, NH_3 reacts with $TiCl_4$ in the absence of moisture, $TiCl_4 \cdot 6\,NH_3$ is formed, which has little obscuring power. Consequently when $TiCl_4$ is used in shells it is generally planned to disperse it with a high explosive, and after a few moments ammonia from a separate compartment is also dispersed. In this manner the total obscuring power [1] is 50 per cent higher than is obtained from $SiCl_4$. The latter is more volatile, therefore more easily handled from a nozzle, and requires a very wet atmosphere for giving its highest obscuring power. Consequently it is better adapted for use in the navy. But in the army, $TiCl_4$ is used in shells and grenades. The production of $TiCl_4$ during the war became an important industry, crowding out for the time the manufacture of titanium pigments. During 1918 it is said that 160 tons of titanium ore were used [2] in the production of tetrachloride for military purposes.

Titanium compounds find a limited use in pyrotechnics, where they increase the intensity of the light. TiO_2 is deposited in minute particles on $CaSO_4$ in the manufacture of linoleum; [3] it was also used in place of SnO_2 as an opacifier in glass and

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[1] The total obscuring power (T. O. P.) is the product of the volume of smoke in cubic feet produced by 1 pound of the substance, multiplied by the density of the smoke. The density is the reciprocal of the depth of smoke layer in feet, beyond which it is impossible clearly to distinguish the filament of a 40-watt Mazda lamp. The T. O. P. of phosphorus varies from 3000 to 16,000, depending on the humidity.

[2] See *Trans. Am. Electrochem. Soc.* **35** 323 (1919).

[3] *Brit. Pat.* 110, 324.

enamels; the nitride may become useful for the fixation of atmospheric nitrogen as well as for a refractory. Clear crystals of rutile are used as gems; " siloxide " quartz contains some TiO_2 along with ZrO_2, the product being somewhat more satisfactory at high temperatures than ordinary quartz. Pure titanium rods are employed in astronomy for the production of spectra.

Compounds. — Titanium forms four distinct classes of compounds whose relationships are shown in Table XXV. In general the compounds resemble those of zirconium, columbium, and tantalum. The oxide, TiO_2, is a little more acidic than ZrO_2, and most of the titanium compounds easily yield a difficultly soluble basic salt, consequently the presence of free acid is essential to complete solution.

TABLE XXV

Classes of Titanium Compounds

OXIDE	HYDROXIDE	CHARACTER	TYPICAL SALTS	NAMES	REMARKS
TiO	$Ti(OH)_2$	Basic only	$TiCl_2$, TiS, $TiSO_4$	Dichloride Monosulfide, etc.	Easily oxidized; not important
Ti_2O_3	$Ti_2O_3 \cdot X(H_2O)$	Basic only	$TiCl_3$, Ti_2S_3, $Ti_2(SO_4)_3$, etc.	Titanous (or tri)chloride, sesquisulfide, etc.	Easily oxidized and strongly hydrolyzed
TiO_2	$Ti(OH)_4$	Feebly basic	$TiCl_4$, TiS_2	Titanic (or tetra) chloride, disulfide, etc.	Few salts of weak acids; forms complex salts
		Acidic	Na_2TiO_3 $FeTiO_3$	Titanates	Stable compounds; forms complex titanates

Hydrogen appears to combine directly[1] with titanium, but the successful preparation of TiH_4 has only recently been accomplished.[2] It is best prepared by the electrolysis of a dilute solution of H_2SO_4 with a titanium cathode. It is a colorless, odorless gas, which burns readily, and in Marsh's test leaves a residue varying from black to brown, gradually becoming greenish.

With oxygen titanium forms TiO, Ti_2O_3, and TiO_2; other oxides, Ti_3O_4, Ti_7O_{12}, Ti_2O_5, and TiO_3, are described, but their existence is doubtful.

TiO is formed by reduction of TiO_2 with carbon or a metal like zinc or magnesium: $2\ TiO_2 + Mg = MgTiO_3 + TiO$. This reaction shows that TiO_2 is more difficult to reduce than SiO_2. $Ti(OH)_2$ is a black precipitate formed when an alkali is added to a solution of $TiCl_2$.

Ti_2O_3 is formed by reducing TiO_2 with hydrogen or when the vapors of HCl and $TiCl_4$ are passed over white hot TiO_2.

TiO_2 may be prepared artificially in the three crystalline[3] forms, since anatase is the stable form below 860°, brookite between 860° and 1040°, and rutile above 1040° C. The amorphous TiO_2 is prepared by precipitation of a quadrivalent salt with ammonia or by igniting ilmenite with chlorine and hydrogen chloride: $2\ FeTiO_3 + 4\ HCl + Cl_2 = 2\ FeCl_3 + 2\ TiO_2 + 2\ H_2O$. From this mixture $FeCl_3$ is removed by distillation. TiO_2 is insoluble in water and difficultly soluble in acids, but it dissolves in sulfuric acid when heated. On fusion with the alkalies or alkali carbonates it forms titanates.

Orthotitanic acid, presumably $Ti(OH)_4$, forms a gelatinous white precipitate when ammonia, the alkalies, or alkali carbonates are added to a cold solution of a titanate in HCl. When first formed it is soluble in dilute acids, but on standing, and especially on heating, it is gradually dehydrated, forming more sparingly soluble hydrates. On ignition it glows, yielding TiO_2.

Metatitanic acid, $TiO(OH)_2$, is formed by heating a solution containing $Ti(OH)_4$ or a titanic salt, or by action of nitric acid on the element. $Ti(SO_4)_2$ is easily and completely hydrolyzed on boiling. The meta acid is a soft white powder, insoluble in hydrochloric acid, forms colloidal solutions readily, and when ignited yields TiO_2 without glowing.

When H_2O_2 is added to a titanic solution a yellow color is produced, generally ascribed to the formation of derivatives of the superoxide, TiO_3. These pertitanites may, however, be related to Ti_2O_5.[4] Other derivatives have been formed,[5] such as $Na_2O_2 \cdot TiO_3 \cdot 3\ H_2O$, $BaO_2 \cdot TiO_3 \cdot 5\ H_2O$.

With nitrogen titanium reacts vigorously, forming a compound now considered[6] TiN, though various formulæ were formerly assigned to it. It is also prepared by heating a mixture of TiO_2 and carbon in the presence

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[1] E. A. Schneider, *Z. anorg. Chem.* **8** 81 (1895).

[2] A. Klauber, *Z. anorg. allgem. Chem.* **117** 243 (1921).

[3] See Knop, *Jahrbuch Min.* 1877, 408; Daubree, *Compt. rend.* **29** 227 (1849), **30** 383 (1850), **39** 153 (1854).

[4] M. Billy, *Compt. rend.* **172** 1411 (1921).

[5] Melikoff and Pissarjewski, *Ber.* **31** 678, 953 (1898).

[6] Ruff and Eisner, *Ber.* **38** 742 (1905); **41**, 2250 (1908).

of nitrogen or TiO_2 with ammonia. It is as hard as diamond, and exceedingly refractory. A nitride, Ti_3N_4, is also formed,[1] but no nitrate, other than the basic salt, $5\ TiO_2 \cdot N_2O_5 \cdot 6\ H_2O$.[2]

With fluorine titanium forms TiF_3 and TiF_4. The former is produced when K_2TiF_6 is ignited in a stream of hydrogen or when the same substance in solution is reduced by zinc and HCl or sodium amalgam.

TiF_4 is best prepared by the action of anhydrous hydrogen fluoride on titanium or titanium tetrachloride. It unites with the metallic fluorides, forming sparingly soluble titanifluorides of the type M'_2TiF_6 and $M''TiF_6$, which are isomorphous with the similar silicon, zirconium, and tin double fluorides. It does not combine directly with HF, but yields additive compounds with ammonia and pyridine.

With chlorine titanium forms three classes of compounds in which it is bivalent, trivalent, and quadrivalent.

$TiCl_2$ is formed by reduction or heating of $TiCl_3$, which yields a mixture of $TiCl_2$ and $TiCl_4$. The latter may be distilled off. The properties of the dichloride vary considerably with the method of preparation.

$TiCl_3$ is produced by the reduction of the tetrachloride with hydrogen or a metal like silver or mercury. When heated in the air it breaks up, giving the volatile tetrachloride and the solid dichloride. $TiCl_3$ is deliquescent, forms a reddish violet solution with water, and violet crystals, $TiCl_3 \cdot 6\ H_2O$, from a hydrochloric acid solution. An unstable green hydrate of the same composition is formed when an aqueous solution of the trichloride is covered with ether and saturated at 0° with HCl. From the violet form all the chlorine may be removed by $AgNO_3$, but this is probably not true of the green modification. The trichlorides of chromium and vanadium likewise are known in two forms. $TiCl_3$ forms double salts with the chlorides of rubidium and caesium. It is a more powerful reducing agent than stannous chloride and on this account finds extensive application in both qualitative and quantitative analysis.

$TiCl_4$ is prepared by passing chlorine, carbon tetrachloride, or chloroform over the metal, its carbide, the ferrotitanium, or a mixture of the oxide and carbon. The crude $TiCl_4$ may be separated by fractional distillation from $SiCl_4$.

Titanium tetrachloride is a colorless mobile liquid which has a specific gravity of 1.76 at 0°; it freezes at $-23°$ and boils at 136°. It is hydrolyzed by water, forming a series of oxychlorides. In spite of its hydrolysis $TiCl_4$ dissolves in water to a clear solution because enough HCl is formed to prevent the precipitation of $Ti(OH)_4$. On boiling the precipitate appears. The chloride dissolves readily in HCl, apparently forming H_2TiCl_6. On adding NH_3 or organic bases to this solution crystals of the type $(NH_4)_2TiCl_6$ are formed. The chloride forms many stable additive compounds with non-metallic chlorides such as: $TiCl_4 \cdot PCl_3$; $TiCl_4 \cdot PCl_5$; $TiCl_4 \cdot POCl_3$; $TiCl_4 \cdot 2\ POCl_3$, etc. Additive compounds are also formed with ammonia and organic substances.

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[1] Ruff and Treidal, *Ber.* **45** 1364 (1912).

[2] Merz, *Jour. prakt. Chem.* **99** 157 (1866).

With the other halogens titanium forms $TiBr_3$, $TiBr_4$, $TiCl_2Br_2$, $TiClBr_3$, TiI_2, TiI_3, TiI_4.

With carbon titanium combines directly, forming TiC, which is a metallic appearing substance used somewhat in artificial lighting. If nitrogen is present also, a cyanonitride, probably $Ti(CN)_2 \cdot 3\,Ti_3N_2$, is formed. Titanium forms simple or double salts with many organic acids, such as formic, acetic, oxalic, tartaric, thiocyanic, and thiocyanuric.

With sulfur titanium forms the three sulfides, TiS, Ti_2S_3, and TiS_2, besides corresponding normal, basic, and double sulfates. The ability to form sulfates distinguishes titanium rather sharply from silicon and germanium.

TiS is a very stable compound formed by the reduction of the higher sulfides with hydrogen at high temperatures. It is a dark red metallic appearing substance, resembling bismuth. It is unaffected by dilute acids or alkalies, but it is slowly oxidized by nitric acid and aqua regia and dissolved by concentrated sulfuric acid.

Ti_2S_3 is produced when TiS_2 is moderately heated in hydrogen; or when TiO_2 is heated to bright redness in moist H_2S and CS_2 vapor; or when TiN is heated with sulfur and hydrogen. It is a black metallic powder, insoluble in dilute acids but dissolved by concentrated sulfuric and nitric acids.

TiS_2 is formed by the action of CS_2 upon TiO_2; by heating TiO_2, sulfur, carbon, and sodium carbonate; or in purer form by passing $TiCl_4$ vapor with H_2S through a heated porcelain tube. It dissolves in acids with difficulty, and decomposes in boiling potash, giving potassium sulfide and titanate.

$Ti_2(SO_4)_3$ is prepared by reducing TiO_2 with sulfuric acid and heating with an excess of the acid. It forms typical alums with the alkali sulfates and other more complex double sulfates like $3\,Ti_2(SO_4)_3 \cdot Rb_2SO_4 \cdot 24\,H_2O$ and $3\,Ti_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 18\,H_2O$.

$Ti(SO_4)_2 \cdot 3\,H_2O$ has been described,[1] but its existence is doubtful. The basic sulfate, $2\,TiO_2 \cdot 3\,SO_3 \cdot 3\,H_2O$, and the titanyl sulfate, $TiOSO_4$, are definite compounds related to the normal titanic sulfate.

Titanium also forms such compounds as TiP, $TiO_2 \cdot P_2O_5$, and $TiSi_2$.

Detection. — Titanium compounds do not color the Bunsen flame, but show a number of spectral lines in the blue and green region. The borax or phosphate bead is colorless in the oxidizing flame, and after heating in the inner flame is yellow while hot and violet when cold.

All titanic salts are hydrolyzed on dilution and boiling, especially in the presence of $Na_2S_2O_3$, but not in the presence of citric and tartaric acids. If KOH is added to a cold titanic solution, $Ti(OH)_4$, easily soluble in acids, is precipitated; but if the solution is hot, $TiO(OH)_2$, more difficultly soluble, is formed.

$K_4Fe(CN)_6$ gives a brown precipitate from slightly acid solutions.

H_2O_2 produces a yellow or orange-red color when added to a slightly acid solution of a titanic salt. Vanadic salts must be absent.

Thymol added to a sulfuric acid solution of titanium produces an intense blood-red color.

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[1] Glatzel, *Ber.* **9** 1829 (1876).

A titanic salt in acid solution may be reduced to the trivalent condition by zinc or tin. The solution is violet in concentrated solutions, pink in dilute. Dihydroxymaleic acid gives a dull yellow-brown color, which becomes a brilliant orange by oxidation.

TiO_2 is not volatile when heated with H_2SO_4 and HF.

Cupferron precipitates titanium.[1]

Estimation.[2] — Titanium is determined gravimetrically as TiO_2. It is precipitated as the hydroxide with ammonia or by hydrolysis of the salts; or precipitation may be accomplished with cupferron after removing iron.[3]

Estimation may be made colormetrically[4] by adding H_2O_2 to the solution and comparing with the color of a standard titanium solution.

Volumetric determination may be made by reducing the titanium to the trivalent condition with zinc and then titrating with potassium permanganate, ferric chloride, or methylene blue.[5]

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[1] *Jour. Am. Chem. Soc.* **42** 1439 (1920); *Jour. Ind. and Eng. Chem.* **12** 344 (1920); *Analyst*, **44** 307 (1919).

[2] See Hillebrand, *Jour. Am. Chem. Soc.* **39** 2358 (1917); also, *ibid.* **42** 36 (1920); Ettele, *Chem. Analyst*, **27** 10 (1918); Cavazzi, *Ann. chim. applicata*, **11** 94 (1919); C. Grandjean, *Chemie et industrie*, **8** 46 (1922).

[3] Waddell, *Analyst*, **44** 307 (1919).

[4] Cavazzi, *Ann. chim. applicata*, **12** 105 (1919); T. Dieckmann, *Z. anal. Chem.* **60** 230 (1921).

[5] F. Ferreri, *Giorn. chim. ind. applicata*, **2** 497 (1920); *C. A.* **15** 2261 (1921).

CHAPTER IX

GROUP IV — ZIRCONIUM[1]

Historical. — When studying some samples of the mineral zircon from Ceylon, Klaproth in 1789 found a large amount of an oxide which resembled alumina closely but differed from it in being insoluble in alkalies. It proved to be the oxide of a new metal to which the name zirconium was applied from the mineral zircon, which name is probably a corruption of jargon, a Persian word meaning gold-colored. Berzelius studied the element and its compounds, which he supposed were trivalent. He first prepared the metal as an iron gray powder in 1824 by reducing potassium fluozirconate with potassium. The crystalline metal was first prepared by Troost in 1865. In 1857 Deville and Troost determined the vapor density of the chloride and established the quadrivalence of the element. The homogeneity of zirconia has been frequently questioned because of the complex mixtures in which the element is found in nature, the difficulty in the preparation of pure materials and the ease with which zirconium forms widely divergent basic compounds. In 1845 Svanberg reported the new earth noria; in 1864 Nylander believed he had separated two new oxides from zirconia; in 1869 Sorby announced the discovery of jargonia and Church found the new element nigrium; in 1901 Hofmann and Prandtl claimed to have separated euxenerde from the zirconia of euxenite. Each of these announcements has failed of confirmation, and zirconium is commonly regarded[2] as a distinct chemical individual.[3]

The chemistry of the element has developed very slowly because previous to 1892 the main source of supply was the scarce mineral zircon, which is very refractory. With the discovery of baddeleyite, a natural oxide, in 1892 a much larger supply of material became available, and its extraction has been greatly simplified.

Occurrence.[4] — The chief zirconium minerals are zircon, an orthosilicate, $ZrSiO_4$, and baddeleyite, ZrO_2, with traces of

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[1] See "Zirconium and Its Compounds," by F. P. Venable, *Am. Chem. Soc. Monograph* (1922).

[2] Hauser and Wirth, *Ber.* **42** 4443 (1909) and **43** 1807 (1910).

[3] The announcement was recently made of the separation of another element from zirconium. Coster and Hevesy (see *Nature*, Jan. 20, 1923, p. 79) have separated from zirconium material a substance whose X-ray spectrum lines coincide closely with the position which should be occupied by the lines of the element whose atomic number is 72. They have named the new element hafnium, from Hafniae, a name for Copenhagen. They report that most zirconium ores contain 0.01 to 0.1% hafnium, but a Norwegian ore contained about 1% of the new element. Its atomic weight is somewhere between 120 and 181.

[4] See W. T. Schaller, *Min. Resources of U. S.*, 1916, part II, pp. 377–386.

the oxides of iron, calcium, titanium, thorium, and many other elements. Zircon forms tetragonal crystals with a density 4.6–4.8 and hardness 7.5. They are colorless, red, yellow, brown, blue, or green. The more delicately colored ones are used as gems under the names hyacinth, jargon, jacinth, or Matara diamond. Zircon is found chiefly in Ceylon, the Ural Mountains, Greenland, Australia, the Carolinas,[1] Virginia, New York, and Colorado. The mineral baddeleyite, similar to brazilite or zirkelite,[2] is found mainly in Ceylon and Brazil. Extensive deposits, as yet undeveloped, exist in the Caldas region of Brazil,[3] where it is mixed with zirconium silicate. Isolated bowlders weighing as much as 30 tons are described.

In addition to these minerals, zirconium is found in several rare minerals which are mainly silicates, less commonly titanates and tantalates. It is widely distributed in various igneous rocks and is a frequent constituent of rare earth minerals. It has been found in spring water and in the solar spectrum. It is doubtless present in small quantities in many materials in which its presence is not suspected because of the lack of a delicate and characteristic test.

The production of zirconium minerals has never been extensive, nor has the supply been uniform. The United States production has come almost entirely from the North Carolina deposit, which rarely produces more than a ton per year, though in 1883, 26 tons were reported. The exportation from Brazil also shows a wide fluctuation, varying from 7 tons in 1903, to 1119 in 1913, and 8 tons in 1915. The demand during 1920 was brisk, due to increasing interest in zirconia. During the first half of the year zirkite ranged in price from 4½ to 7 cents per pound wholesale, but during the latter part of the year the price fell to 3½ to 4 cents per pound.

Extraction. — From zircon[4] extraction may be made by several methods: (1) fusion with acid potassium fluoride and ex-

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[1] See J. H. Pratt, *N. Car. Geol. Surv. Bulletin* 25 (1916).

[2] The names of these ores are used loosely, especially in commercial circles. Baddeleyite is ZrO_2; brazilite is the Brazilian dioxide, mixed with varying amounts of zirkelite, which is $(CaFe)O \cdot 2(ZrTiTh)O_2$, zircon, and a new unnamed silicate. The term zirkite is a trade name, applied to the partially purified ore; this name does not appear in the 1922 edition of Dana's Mineralogy.

[3] See Miller and Singewald, *The Mineral Deposits of South America*, McGraw-Hill Company (1919).

[4] Zircon may be more easily ground to a powder if the ore is first heated strongly and then plunged into cold water.

traction with hot water; potassium fluozirconate crystallizes on cooling; (2) fusion with potassium bisulfate and extraction with dilute boiling sulfuric acid; the basic sulfate is left undissolved; (3) heating with NaOH and NaF and extracting with water, the sparingly soluble sodium zirconate is dissolved in HCl and on evaporation $ZrOCl_2$ separates; (4) fusion with Na_2CO_3 and extracting with water. The zirconate is dissolved in HCl or H_2SO_4.[1]

The preparation of zirconium material from baddeleyite usually consists in the removal of iron, silica, and less commonly titanium. Fe_2O_3 is present in amounts varying from 0.82 per cent to 10.26 per cent, silica 0.19 to 26.30, and titania from a trace to 3.12 per cent. The method of treatment depends upon the purity desired in the product. (1) Boiling with strong HCl or H_2SO_4 removes most of the iron and titanium; ignition with HF and H_2SO_4 removes the silica. (2) For a product free from impurities, it is recommended that the ore be fused with Na_2CO_3 and $Na_2B_4O_7$.[2] The melt is extracted with water and the zirconium salt crystallized out. (3) Fusion with NaOH[3] in an iron crucible following by extraction with water and HCl, then precipitation of basic zirconium sulfate yields a pure product. (4) Fusion with $BaCO_3$ at 1400° for 2 hours gives barium zirconate, which may be dissolved in HCl and the solution evaporated to remove silica. Dissolve the zirconium in acid and allow $ZrOCl_2$ to crystallize. (5) By heating the ore in the electric arc with carbon the non-volatile zirconium carbide is formed and is easily separated from the volatile silicon carbide. Aqua regia is used to dissolve the ZrC. (6) A method recommended[4] for the large scale purification of zirkite consists in mixing the ore with sufficient carbon to form silicon carbide, then heating in an arc furnace to a temperature above 2220°. This removes 90–95 per cent of the silicon, but no iron. Next the material is heated in the presence of chlorine or phosgene to remove iron.

Separation. — The zirconium compounds prepared from the ores almost invariably contain iron, which is difficult to remove completely. Several methods are available for separating iron

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[1] *U. S. Pat.* 1,261,948, April 9, 1918, claims that by a similar method 99.5 per cent ZrO_2 may be obtained.

[2] See also Jackson and Shaw, *Jour. Am. Chem. Soc.* **44** 2712 (1922).

[3] Rossiter and Sanders, *Jour. Soc. Chem. Ind.* **40** 70 T (1921).

[4] J. C. Thompson, *Proc. Am. Electrochem. Soc.* **50** 445 (1921).

and zirconium. (1) $Na_2S_2O_3$, added to a boiling hot solution of zirconium salt which contains a little free acid, precipitates zirconia, thoria, and titania, but iron, aluminium, and the rare earths are not precipitated. (2) $(NH_4)_2S$ in the presence of tartaric acid precipitates iron but not zirconium. (3) Ether extracts $FeCl_3$ from a solution containing HCl, but not $ZrCl_4$. (4) Repeated crystallizations of the oxychlorides will separate iron and zirconium. (5) Vaporization of $FeCl_3$ at 200° C. (6) Phenyl hydrazine and sulfurous acid precipitate zirconium but not iron.

Zirconium may be separated from titanium by (1) boiling with dilute sulfuric and acetic acids, titanium being precipitated; (2) reducing titanium to the trivalent condition and precipitating potassium zirconium sulfate; (3) precipitating basic zirconium phosphate with hydrogen peroxide and sodium phosphate.

Zirconia may be separated quantitatively from silica by fusion with Na_2CO_3; extract the melt with water, filter, evaporate with nitric acid, dehydrate the silica, and expel it with HF and H_2SO_4.

Titanium and tin may be removed from zirconium by fusion with large excess of $KHSO_4$; dissolve in water and nitric acid, and ignite the SnO_2 residue. Carefully neutralize the solution and precipitate the zirconium with H_2O_2 and from the filtrate precipitate the titanium with NH_4OH.

Metallurgy. — Pure zirconium is difficult to obtain for several reasons: the oxide is very stable and does not decompose except at a temperature at which the reoxidation of the metal is prevented with difficulty; zirconium combines readily with oxygen, nitrogen, hydrogen, boron, silicon, and alloys readily with metals which might serve as reducing agents such as magnesium or aluminium.

The attempts to prepare metallic zirconium have been made by the same methods and with much the same results as those used in the reduction of titanium. The most important investigations are as follows: (1) Berzelius reduced[1] potassium fluozirconate with potassium and obtained an amorphous powder which must have contained much oxygen. (2) Troost[2] passed the vapor of $ZrCl_4$ over heated sodium or magnesium and

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[1] *Pogg. Annalen* 4 117 (1824).

[2] *Compt. rend.* 61 109 (1865

obtained a fairly pure metal in powder form. (3) Weiss and Neumann obtained[1] the element by reducing potassium fluozirconate with sodium in an iron bomb containing NaCl. Their product contained 97–98 per cent zirconium and when used as electrodes in a vacuum arc, the practically pure metal was obtained. By replacing the sodium with aluminium a coherent product 99.8 per cent pure was obtained.[2] (4) The anhydrous chloride may be reduced[3] in a vacuum with sodium. (5) The oxide is pretty successfully reduced with magnesium,[4] or carbon at the high temperature of the electric furnace,[5] or calcium in an evacuated iron dish.[6]

The rapid progress being made in the development of the chemistry of zirconium leads to the prediction[7] that the metal in powder form will soon be available in semi-commercial quantities at a price of about $12 per pound for material 95 per cent pure.

Properties. — Many conflicting statements are made in regard to the properties of zirconium. This fact is easily understood when it is remembered that the pure element has rarely if ever been prepared, and many statements are based on the conduct of alloys or mixtures. Formerly it was stated that the element exists both in a crystalline and amorphous (or graphitic) condition, but this statement is yet to be proven with pure material. The purest zirconium is known as a black amorphous powder, which burns brilliantly when heated to a high temperature in the air. The heat of combustion is given as 1958.7 calories per gram. It is oxidized when fused with alkali nitrates, carbonates and chlorates, but is only slightly attacked by acids. When the impure powder is pressed into pencils and heated in hydrogen at low pressure, the metal melts, forming steel-gray drops which take a high polish. The hardness of the compact metal is still open to question, Moissan reporting 4.7, Marden and Rich[8] 6.7, and others giving values as high

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[1] Weiss and Neumann, *Zeit. anorg. Chem.* **65** 248 (1910); see also *ibid.* **99** 123 (1917).

[2] Marden and Rich, *Jour. Ind. and Eng. Chem.* **12** 651 (1920).

[3] Lely and Hamburger, *Zeit. anorg. Chem.* **87** 209 (1914).

[4] Phipson, *Compt. rend.* **61** 745 (1865).

[5] Moissan, *Compt. rend.* **116** 1222 (1893).

[6] Wedekind, *Annalen* **395** 149 (1913).

[7] H. C. Meyer, *Eng. and Min. Jour.* **111** 151 (1921).

[8] Marden and Rich, *loc. cit.*

as 7 or even 8. The statement that it is hard enough to scratch quartz or rubies probably refers to material containing considerable carbide. Determinations of the melting point vary from 1530° (Burgess) to 2350° (Von Bolton); recent specific heat determinations vary from 0.0656, giving an atomic heat of 6.19, to 0.0804 corresponding to an atomic heat of 7.31, the highest atomic heat assigned to any substance. The metal has been reported both paramagnetic and diamagnetic.

Zirconium burns readily in air, the powder form more readily than the compact form. The affinity for oxygen is so strong that zirconium will reduce the oxides of lead, copper, boron, titanium, and silicon. The oxide is very stable. Zirconium combines with hydrogen when heated below 700°, but at 800° the hydrogen is completely expelled; a nitride is formed when the metal is heated in the air or in ammonia, but this compound does not exist above 1000°; it also forms a carbide, a silicide, and a boride by direct union of the elements; chlorine and bromine form tetrahalides and sulfur combines with the hot metal. Zirconium is slowly dissolved by hot HCl and H_2SO_4; HNO_3 has very slight action, it is rapidly oxidized by aqua regia, and hydrofluoric acid is its best solvent. The impure metal dissolves in alkaline solution with the evolution of hydrogen, but the pure metal does not.[1] Fused alkalies attack zirconium somewhat, while fused KNO_3 reacts with it vigorously.

The compounds of zirconium are frequently found to be radioactive, but this is probably due to the presence of related radioactive substances, especially thorium.

Uses. — Up to the present, there have been few suggested uses for metallic zirconium. A form of pure metal which is malleable has recently been mentioned as possessing properties making it an interesting substitute for platinum. But no definite announcements have been made. Formerly zirconium filaments were used [2] to some extent in electric lamps, but they have not been successful, because of the difficulty in preparing the pure metal. The electrical conductivity, high fusion point, and high emissive power make such filaments very efficient. The marked affinity which zirconium has for oxygen has suggested its use as an efficient reducing agent in the

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[1] Wedekind and Lewis, *Ann.* **371** 366 (1910).

[2] *Zeit. angew. Chem.* **23** 2065 (1910).

preparation of other metals; it should also make a valuable scavenger.

The principal uses to which zirconium has been put are in its alloys and in certain of its compounds. Doubtless the most promising of these alloys is ferrozirconium,[1] which may be made by reduction of a mixture of zircon and iron ore in an electric furnace; by fusion of a mixture of zircon, cast iron, lime, and fluorspar;[2] or by the reduction of the mixed oxides with aluminium. As usually prepared, they contain about 30–40 per cent zirconium, with small amounts of carbon, aluminium, and titanium usually present. If a low-carbon product is desired, reheating the ordinary ferrozirconium with TiO_2 is recommended.[3] Some of these alloys are resistant [4] to oxidation and chemical corrosion, and are sufficiently malleable and ductile to permit their use as filaments in incandescent lamps. Another alloy containing 10–40 per cent iron and 60–90 per cent zirconium, with a little titanium to increase toughness, is recommended [5] for lamp filaments, spark points, and transformer elements. Ferrozirconium has been used [6] as a scavenger in the purification of steel in the same manner as ferrotitanium, but it seems to have no advantage over the latter. Zirconium steel [7] has recently attracted some attention. It is known that just before the outbreak of the recent war the Krupps were experimenting with alloy steels containing a small amount of zirconium. These steels are said to be well adapted for use as armor plate and armor-piercing projectiles [8] and for high speed tools.[9] During the excitement of the war period extravagant statements were made concerning the efficiency of zirconium steel for use in making light armor plate. Later studies [10] indicate that as much as one per cent of zirconium has little effect, either good or bad, upon the properties of steel.

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[1] See *U. S. Pat.* 1,401,265, Dec. 27, 1921.

[2] *U. S. Pats.* 1,401,265–7, 1921.

[3] *U. S. Pat.* 1,374,037, April 5, 1921.

[4] *U. S. Pat.* 1,151,160.

[5] *U. S. Pat.* 1,248,648.

[6] See Schaller, *U. S. Geol. Surv. Min. Res.* II, 25 (1916).

[7] See *U. S. Pats.* 1,401,266; 1,401,267, Dec. 27, 1921; and 1,374,038, April 5, 1921.

[8] *Iron Age*, May 3, 1917, p. 1073.

[9] Manning, *Min. and Sci. Press*, June 29, 1918, p. 883.

[10] See Note, Bureau of Standards, *Chem. and Met. Eng.* **26** 190 (1922).

A series of alloys of zirconium and nickel, free from iron and carbon, is called "cooperite," and shows some valuable properties for the preparation of cutting tools.[1] The alloy may be cast and only a little grinding is required for finishing. The tools are self-hardening, so no tempering is needed, and since the alloy has a high heat conductivity the tools are unusually efficient for high speed work. The hardness is increased by increasing the amount of zirconium. An alloy containing 2-10 per cent zirconium takes a fine cutting edge, but if the zirconium is increased 16-30 per cent the alloy is very hard, but its melting point and tensile strength are lowered. If molybdenum is added the melting point is raised. Zirconium alloys are also serviceable for increasing the strength and resistance to corrosion of brass and bronze, since small quantities aid in securing sound castings.

Other zirconium alloys which have been prepared and studied somewhat are those with cobalt, aluminium, magnesium, and silver. Zirconium apparently forms no alloys with tin, lead, or the metals of the alkali or alkaline earth groups.

The oxide has been used in a variety of ways and is at present by far the most promising zirconium material from the standpoint of commercial applications. The properties which make it especially valuable are its very high melting point, its resistance to corrosion even at high temperatures, its low porosity, low heat conductivity, and the low coefficient of expansion. These are the properties of an almost ideal refractory, but unfortunately a very small per cent of impurities in the zirconia modify these properties materially, and the preparation of the pure oxide is still an expensive process.

Zirkite brick for furnace linings has been on the market for some time. The use of this material has been greatly stimulated by war conditions, and the results so far obtained show clearly the importance of zirconia as a refractory. Due to its low coefficient of expansion (linear coefficient of expansion for pure material is 0.00000084 compared to 0.0000007 for quartz), it is especially serviceable in furnaces requiring extremes of temperature with sudden changes. A small experimental furnace lined with zirkite material is reported to have shown no noticeable deterioration after 150 heats of 2-3 hours each at

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[1] *U. S. Pats.* 1,221,769 (1916); 1,277,046 (1918); 1,387,663 (1921).

temperatures of 1400°–1600° C. Both heating up and cooling off were done rapidly.

In addition to its use as entire refractory brick, some success has been accomplished with zirconia as a coating for other refractory materials. One Martin-Siemans furnace was tested[1] out in Europe and gave excellent satisfaction for seven or eight months, representing a saving of 50 per cent in the maintenance cost, though the initial cost was high.

Very interesting results have also been obtained with the use of zirconia in crucibles, muffles, and other high temperature utensils. The material is put together with various binders, such as gelatinous $Zr(OH)_4$, starch, phosphoric acid, glycerine, tar, borates, or silicates, depending on the purpose for which the utensils are to be used. Sometimes magnesia and other refractory materials are mixed with the zirconia. These dishes are dried for several days, then fired at 2000°–3000°, when a ware is obtained which is impervious to most liquids and resistant to many fusion mixtures. On account of the low thermal conductivity the walls are made much thinner than when clay is used. It has been shown by "accelerated action" tests that zirconia crucibles at temperatures of 1200°–1600° C. withstand successfully the corrosive action of acid slags containing manganous and ferrous oxides, glass of various kinds, and cobalt-nickel speiss. Resistance to corrosion is somewhat less marked in the case of litharge, Portland cement, copper oxide, ferric oxide, or any basic slag. The zirconia is unsuited for use with iron sulfide, sodium hydroxide, or carbonate, cryolite, fluorspar, or any charge yielding vapors of fluorine or hydrofluoric acid. Such vapors cause the zirconia to swell and become spongy, while the caustic fusions are absorbed by capillary attraction which causes the material to crack. Bisulfate fusions also attack zirconia.

Laboratory utensils of zirconia are also available for use as crucibles, combustion tubes, muffles, pyrometer tubes, etc. The most serious obstacle to be overcome in the manufacture of this sort of ware is the tendency to crack at high temperatures, due to high shrinkage. The most successful method of overcoming this defect is to fuse the material to a hard, compact mass in an arc furnace, then grind up and mix with a suitable

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[1] L. Bradford, *Chem. Trade Jour.* **62** 284 (1918).

binder, and shape into the desired utensils. This process is said to give a porcelain-like ware which has very useful properties.[1] The efficiency of zirconia crucibles is increased by the addition of 1 or 2 per cent of alumina, thoria, or yttria,[2] especially for use at temperatures 2000°–2400° C. Zirconia ware takes a polish well, but it is difficult to find a suitable glazing material. A mixture of feldspar, alumina, etc., is quite satisfactory. If fired at a sufficiently high temperature, the dishes are quite strong, and capable of withstanding a considerable blow. On account of the low coefficient of expansion the white hot ware may be safely thrust into cold water. It has the advantage also of being free from devitrification.

Recently a brand of silica ware, known as "siloxide," has appeared on the market. It is quartz containing 0.5 to 1 per cent of zirconia with titania, which produces increased resistance to metallic oxides, especially the alkaline oxides. In addition the tensile strength of the ware is increased, and the tendency to devitrification decreased.

The future of zirconia as refractory is still somewhat uncertain. It has highly desirable properties which would make it an ideal material for high temperatures, especially in the electric furnaces. But unfortunately it has some properties which are fatal to its popularity. Accordingly, zirconia refractories are highly praised or vigorously condemned, depending on the viewpoint of the experimenter. The main problems yet to be solved are connected with cost and preparation of a purer material. The refractory should be practically free from iron, titania, and silica. The removal of iron by a method which will be both inexpensive and efficient is probably the most essential step in the development of this refractory[3] since iron acts as a flux. The successful counteraction of the high shrinkage would permit its use *in situ* and accordingly lower its cost and increase its usefulness enormously.

Zirconium dioxide has been used for many years in connection with the problems of artificial lighting because of the brilliant light emitted when it is heated to incandescence. As early as 1830 an attempt was made to light the streets of Paris

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[1] Bayer, *Zeit. angew. Chem.* **23** 485 (1910); Podszus, *ibid.* **30** (I) 17 (1917); Weiss, *Zeit. anorg. Chem.* **65** 220 (1910); Ruff, *ibid.* **86** (1914).

[2] Ruff and Lauschke, *Zeit. anorg. Chem.* **97** 73 (1916).

[3] E. H. Rodd, *Jour. Soc. Chem. Ind.* June 15 (1918).

by the use of incandescent zirconia buttons. The first Welsbach gas mantle was made largely of zirconia, but this material soon was completely replaced by thoria, since the latter glows at a much lower temperature. For a long time zirconia has been used to coat the lime or magnesia pencils in the Drummond light, where it has distinct advantage because of its brilliancy and the fact that it does not absorb carbon dioxide or moisture from the air. Hence, zirconia pencils give a steadier light than either lime or magnesia. Such pencils have been used for automobile headlights, in the Blériot lamps which use zirconia rods heated to incandescence. Nernst proposed to use rods of pure zirconia (or magnesia) in his first attempt to obtain a means of illumination by use of the electric current, which would be superior to the carbon filament lamp. These oxides have the disadvantage of requiring preheating, since they are non-conductors at ordinary temperatures, but when heated to about 634° they have the ability to conduct electricity at ordinary voltages. Later he arranged a shunt circuit with a platinum spiral to effect the preheating, and by using a mixture of the oxides of zirconium, thorium, yttrium, and sometimes cerium he obtained quicker response and more intense light. These oxides are called conductors of the second order,[1] that is, the oxides are actually ionized, the metal migrating to the cathode and oxygen to the anode. The gas escapes, but the metals recombine with oxygen of the air as soon as they are liberated.

Zirconium oxide finds numerous other applications besides its uses as a refractory and in artificial lighting. In ceramics it is an opacifier sold under the trade name "terrar," which came into extensive use during the war as a result of the high cost of stannic oxide. The pure oxide is superior to stannic oxide as an opacifying agent because it is less easily reduced, is less volatile, and produces an enamel which is more resistant to vegetable and fruit acids. Prepared in various ways zirconia is used as a toilet powder, as a polishing powder, as a material for manufacturing small electric furnaces, and under the trade name "kontrastin" it is used for defining the intestines in X-ray studies of digestion. When 15 per cent ZrO_2 is added to porcelain, the strength and electrical resistance at high temperature are improved.

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[1] *Zeit. electrochem.* 6 41 (1899).

Other compounds of zirconium have been used in many ways. Various attempts have been made to use zirconium material as filaments in electric lamps. Metallic zirconium, which can be fused in the electric arc *in vacuo*, gives a satisfactory light, but the cost is very high. Zirconium alloys, especially with iron, have also been tried but unsuccessfully. The most promising zirconium material for this purpose is the carbide, which can be prepared without difficulty and gives an efficient light, but it is unable to compete with tungsten filaments.[1]

Zirconium compounds, such as the oxide, silicate, basic carbonate, phosphate, etc., are useful as white pigments and paint bases. They possess good covering power,[2] mix readily with paint vehicles, are permanent, unaffected by hydrogen sulfide, acids, or alkalies, and have the advantage of being non-poisonous.

Zirconium material in the form of the oxide and other insoluble compounds is incorporated with rubber[3] before vulcanization for the double purpose of accelerating the vulcanization with sulfur and of giving a product of greater toughness and tensile strength.

Zirconium silicate yields a superior spark plug porcelain[4] which has high dielectric strength, great mechanical strength, and is so indifferent to temperature changes that it may be heated to 1300° C. and plunged into ice water without developing cracks.

Zirconium basic acetate has been used for weighting silk; several compounds have been suggested as mordants and in the preparation of lake dyes; the nitrate has been employed as a food preservative; the hard compounds, like the carbide, make effective abrasives; the clear crystalline zircon is used as a gem, the red variety being known as hyacinth, the yellow is called jacinth, the white is known as jargon, the pale brown crystals from Ceylon are decolorized by heat and called Matara diamonds.

Compounds.[5] — Zirconium is essentially quadrivalent in its compounds. The only exceptions to this fact are in the cases

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[1] See Baumhauer, *Zeit. angew. Chem.* **23** 2065 (1910).

[2] See pamphlet by H. A. Gardner, *Circular* 62 (April, 1919), Educational Bureau Paint Manufacturers Ass'n of U. S.

[3] *U. S. Pat.* 1,247,257, Nov. 20, 1918.

[4] G. A. Pritchard, *N. J. Ceramist*, **1** 145 (1921).

[5] For more detailed information concerning recent contributions to some of the compounds of zirconium see *Jour. Am. Chem. Soc.* **41** 1722 (1919); *ibid.*

of the hydride, ZrH_2, the sesquioxide, Zr_2O_3, and the superoxides, Zr_2O_5 and ZrO_3. These compounds do not form salts of the same order and are not well established. Since zirconium is definitely amphoteric, it forms two general classes of compounds, the zirconium salts and the zirconates. The normal zirconium salts, like $ZrCl_4$, do not exist in water solution since they are easily hydrolyzed, giving rise to the zirconyl and basic zirconyl salts which contain the bivalent radical ZrO. Consequently, compounds of this order are more numerous and more important than the normal salts. There is frequently a tendency for several zirconyl radicals to combine with one anion, forming a series of compounds of increasing basicity. This tendency is at times so pronounced that it seems impossible to consider the products as definite chemical compounds. Such substances may be considered as absorption compounds in which the colloidal hydroxide has absorbed the acid radical. There is much confusion when attempts are made to represent the composition of the complex zirconyl compounds by chemical formulæ.

In its compounds, zirconium resembles titanium closely, but differs from it in valence and the degree of acidity of its hydroxide. Its greater basicity is also shown by the formation of a nitrate and carbonate. The fluozirconates resemble not only the corresponding salts of titanium but also those of silicon and tin. Its quadrivalence and basicity suggest thorium and there is also a resemblance to the compounds of germanium.

With hydrogen zirconium forms the bivalent compound ZrH_2 by direct union of the elements at 700° and 1.5 atmosphere pressure; or by reducing zirconia with both hydrogen and magnesium. It is a solid, resembling the hydrides of the alkali and alkaline earth metals more closely than the gaseous hydrides of carbon, silicon, and germanium. The existence of a gaseous hydride of zirconium has been denied.[1]

With oxygen zirconium has been reported as forming a sub-oxide, ZrO, but its existence is doubtful;[2] Zr_2O_3 is formed by burning the hydride in air; hydrated peroxides, $Zr_2O_5 \cdot XH_2O$ and $ZrO_3 \cdot XH_2O$, are formed by precipitation in the presence of H_2O_2. The only important oxide is ZrO_2.

ZrO_2 may be prepared in the laboratory by igniting the hydroxide, nitrate, sulfate, carbonate, or oxalate. When prepared by gentle ignition

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42 2531 (1920); *Zeit. anorg. Chem.* **106** 1 (1919); *Compt. rend.* **167** 201 (1918); *ibid.* **164** 946 (1917); *ibid.* **165** 25 (1917); *Jour. Chem. Soc.* **111** (1) 306 (1917).

[1] Schwarz and Konrad, *Ber.* **54B** 2122 (1921).

[2] Schwarz and Deisler, *Ber.* **52** (B) 1806 (1919).

it is a fine white powder, insoluble in water, easily soluble in acids, but on heating to high temperatures it seems to undergo polymerization and is soluble only in concentrated sulfuric and hydrofluoric acids.

$Zr(OH)_4$, the normal hydroxide, is precipitated in the cold when an alkali hydroxide is added to the solution of a zirconyl salt. It is gelatinous, resembling $Al(OH)_3$ both in appearance and behavior. It is insoluble in water, difficultly soluble in weak acids, readily soluble in strong mineral acids. When dried at ordinary temperatures it loses water continuously, but at 100° the definite compound $ZrO(OH)_2$ is produced, which is unchanged up to 200°. When heated to 300° the material begins to glow, and at higher temperatures there are small explosions as it crumbles to a fine powder, ZrO_2. Zirconyl hydroxide, $ZrO(OH)_2$, is also produced when an alkali is added to a zirconyl solution at a temperature of 85° or more. The hydroxide is almost insoluble in ammonia, but dissolves somewhat in KOH and better in NaOH. The compounds formed are zirconates, but these may be much more easily produced by fusion methods. Colloidal solutions are readily formed, in which the hydrosol is positively charged. The hydrogel has remarkable powers of absorption, as is shown by the fact that it drags down alkalies and retains them tenaciously, while it possesses the ability of removing the cuprammonium complex entirely from solution.

With nitrogen zirconium unites directly, but less readily than does titanium. Several nitrides have been described, but the most definite, perhaps the only, compound formed is Zr_3N_2.[1] This results also when zirconium is heated in an atmosphere of ammonia, or the compounds are reduced in the presence of air. It does not burn in oxygen or chlorine, but evolves ammonia when fused with potash.

The nitrate may be obtained by adding HNO_3 to the hydroxide and allowing the mixture to stand over phosphorus pentoxide and sodium hydroxide. If the solution is evaporated, nitric acid is given off and a basic salt is deposited. Stable crystals of the formula $ZrO(NO_3)_2 \cdot 2\ H_2O$ are formed, but these cannot be dehydrated.

With fluorine zirconium forms ZrF_4 when the oxide is heated with ammonium fluoride or when the chloride is treated with hydrogen fluoride. At 50° its solution begins to suffer hydrolysis, but on evaporating a solution containing free HF, a deposit is obtained to which the formula $ZrF_4 \cdot 3\ H_2O$ was formerly applied. It has some properties of a salt of this composition, but its behavior seems to indicate a composition $ZrOF_2 \cdot 2\ HF \cdot 2\ H_2O$.[2]

Double fluorides are numerous and important. When a moderate amount of KF is added to a solution of ZrF_4, the crystalline precipitate, potassium fluozirconate, K_2ZrF_6, is formed. It is also obtained by fusing zircon with KHF_2; it is used in the purification of zirconium, the preparation of the element and its quantitative determination. Caesium, sodium, ammonium, lithium, thallium, magnesium, zinc, cadmium, manganese, nickel, and copper form similar fluozirconates. Double fluorides of the formulæ $KF \cdot ZrF_4 \cdot H_2O$ and $3\ KF \cdot ZrF_4$ are also formed.

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[1] Wedekind, *Annalen*, **395** 149 (1913).

[2] E. Chauvenet, *Compt. rend.* **164** 630, 727, 816, 864, 946 (1917).

With chlorine the tetrachloride $ZrCl_4$ is formed in many ways such as: (1) heating the carbide with chlorine at 300°; (2) heating ZrO_2 to 800° in a stream of chlorine and carbon tetrachloride; (3) heating the metal in the presence of chlorine or hydrogen chloride; (4) passing a mixture of carbon monoxide and chlorine over ZrO_2, at 400°. $ZrCl_4$ hydrolyzes easily, so it is known only in the anhydrous state. It fumes strongly in moist air and reacts vigorously with water, forming the soluble oxychloride, $ZrOCl_2$. It is a white crystalline solid which sublimes readily. In formation and behavior it strongly resembles the chlorides of the non-metallic elements. Addition products are formed with ammonia, organic bases, and phosphorus pentachloride. It also forms condensation products with esters, organic acids, phenols, etc.

With carbon zirconium unites directly at high temperatures, forming ZrC. This compound may accordingly be prepared by heating zircon with carbon in an electric arc. It is a gray colored crystalline mass, hard enough to scratch glass but not rubies, and it is not decomposed by water even at red heat. In the latter fact the relatively slight electro-positiveness of zirconium is shown, since the carbides of the more active metals are readily decomposed by water, yielding hydrocarbons.

No anhydrous carbonate has been prepared, but basic carbonates like $ZrCO_4 \cdot ZrO_2 \cdot 8\ H_2O$ may be precipitated by adding Na_2CO_3 to the solution of a zirconium salt. The precipitates are soluble in excess of reagent, with the possible formation of double carbonates.

Zirconium forms normal and basic acetates, a basic formate, and several oxalates and tartrates.

With silicon there are formed the silicide $ZrSi_2$, the natural silicate $ZrSiO_4$, and various complex silicates. Native zircon as well as certain other zirconium ores are quite strongly radioactive, and when heated they display luminescence and suffer a change in density and color.[1] Zircon also shows[2] the property of triboluminescence.

With sulfur a compound of the formula ZrS_2 is produced by the action of CS_2 on zirconia at red heat. It forms steel-gray crystals which are not decomposed by water nor most acids, but HNO_3 oxidizes the zirconium and precipitates the sulfur. The zirconyl sulfide ZrOS is obtained when the anhydrous sulfate is heated to red heat in a stream of H_2S. It is a bright yellow powder which ignites readily in the air.

Neutral zirconium sulfate, $Zr(SO_4)_2$, is prepared by heating zirconia with an excess of concentrated sulfuric acid and then expelling the excess acid. This salt dissolves slowly in water with the evolution of heat, presumably forming a tetrahydrate, which may be obtained in crystalline form. The normal sulfate is easily hydrolyzed, yielding a solution with a strong acid reaction. Such a solution yields no precipitate or one that forms slowly when oxalic acid or ammonium oxalate is added, while both these reagents produce an immediate precipitate when added to most zirconium salts. On electrolysis of a sulfate solution zirconium concen-

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[1] See Venable, *Zirconium*, Am. Chem. Soc. Monograph, p. 99 *et seq.* and also, *Jour. Elisha Mitchell Sci. Soc.* **34** 73 (1918).

[2] Karl, *Compt. rend.* **146** 1104 (1908).

trates about the anode, while in a solution of $ZrCl_4$ in HCl the metal goes to the cathode. These peculiarities may be explained[1] by the fact that at certain dilutions there is present in solution acid sulfate (called also zircon-sulfuric acid) of the formula $ZrOSO_4 \cdot H_2SO_4$ which ionizes, giving $2 H^+ ZrO(SO_4)_2^{--}$. This explanation is not, however, in accord[2] with all known facts.

A basic sulfate, $4 ZrO_2 \cdot 3 SO_3 \cdot 15 H_2O$, separates from a dilute solution of the sulfate. This salt has been used for atomic weight determinations. Other basic and complex sulfates are known.

Zirconium also forms a sulfite, $Zr(SO_3)_2 \cdot 7 H_2O$, a selenate, $Zr(SeO_4)_2 \cdot 4 H_2O$, and a selenite, $Zr(SeO_3)_2 \cdot H_2O$, as well as various simple and double phosphates. It also forms salts with oxalic, tartaric, citric, salicylic, and other organic acids.

Detection and Estimation.[3] — Zirconium is distinguished from aluminium and beryllium by the fact that the hydroxide is precipitated by NaOH, KOH, NH_4OH, or $(NH_4)_2S$, but the precipitate is insoluble in excess of the reagent. $(NH_4)_2CO_3$ precipitates the flocculent basic carbonate, which is soluble in excess of reagent but reprecipitated on boiling. An excess of alkali iodate added to a zirconium solution containing HNO_3 precipitates the zirconium quantitatively, leaving the aluminium in solution. Thorium and titanium must be absent.

Zirconium is distinguished from thorium: (1) by the fact that the addition of oxalic acid precipitates the white zirconium oxalate, soluble in excess of the reagent; (2) by the failure of zirconium to form a precipitate with HF; (3) by the formation of basic zirconium sulfate, insoluble in dilute hydrochloric acid, when K_2SO_4 is added to a boiling zirconium solution.

The separation of iron and zirconium is of particular importance, especially on the large scale. (See Separation, p. 151.) For the determination the two oxides may be weighed together and then the iron reduced and estimated by titration. If titanium and zirconium occur together, both may be precipitated by hydrogen peroxide and the titanium determined colorimetrically.[4] Both titanium and columbium may be separated by fractional precipitation of the boiling solution with ammonia.

Zirconia and silica may be separated by heating thoroughly with HF and an excess of H_2SO_4.

Turmeric paper is colored pink or reddish brown by zirconium salts in HCl solution. Ferric salts and titanium should be reduced by zinc. When Na_2HPO_4 is added to a hydrochloric acid solution of zirconium a voluminous precipitate forms. This test may be used in the presence of

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[1] See Ruer, *Zeit. anorg. Chem.* **42** 87 (1904); Hauser, *ibid.* **54** 196 (1907); Rosenheim and Frank, *Ber.* **38** 812 (1905) and **40** 803 (1907).

[2] See Venable, *Zirconium*, Am. Chem. Soc. Monograph, pp. 78–80, 112.

[3] For a splendid discussion of the analysis of zirconium minerals and alloys see *Chimie et industrie*, **2** 385 (1919); also *Zeit. angew. Chem.* **24** (1911); *Zeit. anal. Chem.* **50** 733 (1911); *Thesis* of Heinrich Pope, Fredrich-Wilhelm University (1917), and *Thesis* of Magdalene Hüniger, *ibid.* (1919); Venable, *Zirconium*, Am. Chem. Soc. Monograph, p. 120.

[4] Dittrich and others, *Z. anorg. Chem.* **43** 230 (1904); **56** 337, 344, 348 (1907).

iron, aluminium, titanium, thorium, and the rare earths, and will detect 0.0005 per cent of zirconia.

Pyrogallolaldehyde produces a yellow color or precipitate with thorium salts and the same results with zirconium compounds after boiling or adding H_2O_2.[1]

Cupferron is used for both qualitative detection and quantitative estimation of zirconium.[2]

Zirconium may be precipitated from its solutions as the hydroxide or oxalate, then ignited and weighed as ZrO_2.

Addition of secondary ammonium phosphate to a zirconium solution in 20 per cent H_2SO_4 and in the presence of H_2O_2 precipitates zirconium quantitatively[3] even in the presence of iron, aluminium, chromium, cerium, and thorium. On ignition ZrP_2O_7 is formed.

Zirconium may be determined[4] as the basic sulfate even in the presence of iron and aluminium.

Selenious acid precipitates[5] a basic zirconium selenite which on ignition yields the oxide. This method is satisfactory and may be applied to zirconia ores.

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[1] H. Kaserer, *Chem. Zeit.* **42** 170 (1918).

[2] See *Jour. Am. Chem. Soc.* **39** 2358 (1917); *ibid.* **42** 1439 (1920); and *Jour. Ind. and Eng. Chem.* **12** 348, 562 (1920).

[3] See *Jour. Am. Chem. Soc.* **41** 1801 (1919); *ibid.* **42** 36 (1920); *Compt. rend.* **168** 348 (1919).

[4] Rossiter and Sanders, *Jour. Soc. Chem. Ind.* **40** 70 T (1921).

[5] Smith and James, *Jour. Am. Chem. Soc.* **42** 1764 (1920).

CHAPTER X

GROUP IV — CERIUM AND THORIUM

CERIUM

THE element cerium is inseparably connected with the rare earth group, and it is generally customary to discuss it with the members of Group III. But it differs from the other rare earth elements in forming a well defined series of quadrivalent compounds, resembling thorium quite closely. Because of this relationship, as well as its greater abundance and commercial importance, it seems best to discuss certain phases of the chemistry of cerium with Group IV. The history, occurrence, extraction, and separations are discussed in Chapter VI.

Purification. — Both cerium and thorium usually accompany the rare earths when these elements are extracted from their minerals. The separation of cerium from the other members of the rare earth group usually depends upon the fact that under the influence of oxidizing agents cerium forms quadrivalent compounds in which it is much more feebly basic than in its trivalent state. Since thorium resembles the ceric compounds, it is concentrated along with the cerium. Several methods are used: (1) The solution of the mixed nitrates is poured into very dilute nitric acid when basic ceric nitrate precipitates. (2) Addition of the required amount of potassium permanganate to a nearly neutral solution causes the precipitation of the cerium. (3) Boiling a dilute solution of the nitrates precipitates the basic ceric nitrate; this method is especially effective in the presence of ammonium sulfate or magnesium acetate. (4) Boiling the nitrate solution, which is kept neutral by the presence of marble, with $KBrO_3$ precipitates the basic nitrate very satisfactorily. (5) Separation may also be accomplished by passing a stream of chlorine into a suspension of the hydroxides in sodium hydroxide. The basic ceric hydroxide remains undissolved, while the other rare earths dissolve as chlorides. (6) The double ammonium ceric nitrate is sparingly soluble in nitric acid and may be precipitated by adding NH_4NO_3 to a solution of nitrates containing much free nitric acid.

Thorium may be removed from cerium material by precipitation: (1) with $Na_2S_2O_3$ and boiling; (2) with copper and cuprous oxide when added to a nearly neutral solution of the boiling chlorides; and (3) with ammonium oxalate, after oxidizing the cerous salts to ceric.

Zirconium may be removed by fusing the oxides with KHF_2 and extracting with water acidified with HF. The zirconium dissolves, forming K_2ZrF_6, but both cerium and thorium fluorides are insoluble.

Metallurgy. — Metallic cerium was first prepared in powder form by Mosander, who heated the chloride with sodium. The yield is poor, and the product contaminated with sodium and sodium chloride. Reduction of the fluoride with calcium or aluminium or of the oxide with magnesium, aluminium, calcium, carbon, or silicon yields either an alloy or a compound of cerium. The most successful methods of reduction are by electrolysis. Hillebrand and Norton[1] prepared considerable quantities of the metal by electrolysis of the chloride. This method has been elaborated by a number of workers,[2] and much cerium produced in this way. Electrolysis of the fused fluoride or of the oxide dissolved in the fused fluoride has been successfully tried[3] in Europe.

The purification of cerium is best accomplished according to Hirsch by forming the amalgam and skimming the impurities off from the surface of the molten mass. The mercury may then be distilled away by heating to a higher temperature in a vacuum.

Properties. — Pure cerium is a metal which is malleable, ductile, and soft enough to be cut with a knife. It machines fairly well, but requires care to prevent buckling. It resembles steel in appearance, takes a polish well, and has a density of 6.92. It is a fair conductor of heat, but does not conduct the electric current well, its resistance being 71.6 micro-ohms per centimeter cube at ordinary temperatures. It is paramagnetic,

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[1] Pogg. *Annalen*, **155** 633 (1875); **156** 466 (1875).

[2] See especially Muthmann, Hofer, and Weiss, *Annalen*, **320** 231 (1902); Muthmann and Weiss, *ibid.* **331** 1 (1904); Hirsch, *Jour. Ind. and Eng. Chem.* **3** 880 (1911); **4** 65 (1912); *Trans. Am. Electrochem. Soc.* **20** 57 (1911).

[3] Muthmann and Scheidmandel, *Annalen*, **355** 116 (1907).

its magnetic susceptibility at 18° being 15×10^{-6} C. G. S. units per gram. According to Hirsch the specific heat over the interval 20°–100° is 0.05112, which corresponds to the unusually high value 7.17 for its atomic heat. Cerium is the only metal which has a greater molecular heat than aluminium, consequently it may be used to dissolve the skin of Al_2O_3 which forms on the surface of molten aluminium. The melting point is 635° (Hirsch). In dry air cerium is fairly stable, but it tarnishes quite rapidly in moist air. Its surface may be protected by a coating of hard paraffin or wax. At 160° it takes fire and burns with greater brilliancy than magnesium, involving a large amount of heat. When scraped with a file or knife it emits sparks. It reacts only very slightly with cold water, but at the boiling temperature there is a slow evolution of hydrogen. Cerium burns vigorously in chlorine at 210°–215° and in bromine at 215°–220°. It combines directly with iodine, sulfur, selenium, tellurium, arsenic, antimony, nitrogen, and hydrogen. Its affinity for oxygen is strong enough to permit it to reduce both carbon monoxide and carbon dioxide. It decomposes carbon tetrachloride, so pyrene is useless for extinguishing the burning metal. It is not attacked by concentrated sulfuric acid or sodium hydroxide; it is slowly dissolved by dilute solutions of hydrogen peroxide, ammonium chloride, or potassium chloride; it dissolves readily in both dilute and concentrated nitric or hydrochloric acids and in dilute sulfuric acid.

Uses. — Pure metallic cerium has no commercial uses, but its alloys are both interesting and capable of wide application. The most important of these is the alloy called misch metal, mixed metal, commercial cerium, or simply "cerium." It is essentially a mixture of cerium, lanthanum, neodymium, and praseodymium, but as usually prepared it contains from 1–5 per cent iron and very small amounts of other elements. The most abundant constituent is cerium, which sometimes runs as high as 70 per cent or more, though generally it is about half of the mixture. The alloy is produced from the rare earth residues of monazite sand. This mineral is used in large quantities for the manufacture of incandescent gas mantles (see Thorium: Uses), which usually contain 99 per cent thoria and 1 per cent ceria. The composition of various monazites is shown in Table XXVI.

TABLE XXVI

Composition[1] *of Some Monazite Sands showing Typical Analyses of Material from Different Sources*

	CEYLON	NIGERIA	INDIA	BRAZIL	CAROLINA[2]	GENERAL AVERAGE BY H. S. MINER
ThO_2	9.45–28.20	3.20– 8.00	10.22– 8.65	6.06	4.32	5
CeO_2	27.15–20.65	36.53–30.50	31.90			
La_2O_3,			61.11	62.12	34.32	30
Di_2O_3, etc.	29.59–21.63	30.00–28.80	28.00		31.24	30
Yttrium Group Oxides	3.93– 0.94	0.39– 1.43	0.46– 0.62	0.80	1.10	2
Fe_2O_3	0.87– 1.13	1.20– 0.81	1.50– 1.09	0.97		5
Al_2O_3	0.17– 0.29	0.10– 0.20	0.17– 0.12	0.10		
CaO	0.45– 0.10	0.21– 0.17	0.20– 0.13	0.21		
SiO_2	1.67– 6.09	0.63– 1.79	0.90– 1.00	0.75	0.86	
P_2O_5	26.12–20.20	28.29–28.16	26.82– 50.26	28.50	29.30	28
Loss on Ignition	0.48–none	0.20– 0.21	0.46– 0.45	0.38		

From this table it is evident that all monazite contains much more ceria than thoria and since the mantle is mainly thoria a very large part of the ceria is not needed for mantle manufacture. The residue which remains after removal of the thoria contains about 45 per cent CeO_2, 25 per cent La_2O_3, and 15 per cent didymia, the remainder being yttrium earths, samaria, etc. The residue represents 60–65 per cent of the original monazite. Since the total world's consumption of monazite has been estimated as being about 88,000 tons up to 1918, it is evident that the supply of cerium material has been very large. Some firms have stored enormous quantities of these rare earth salts, and others have thrown them away. The residues are transformed to the chlorides, which are carefully dehydrated to prevent the formation of basic salts. The purity of the chlorides is not important, but the phosphorus and sulfur content must be low, and iron and aluminium should not be present in more than small amounts. A mixture of the

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[1] Analyses by S. J. Johnstone, *Jour. Soc. Chem. Ind.* **33** 56 (1914).

[2] J. H. Pratt, *N. Car. Geol. Surv. Bull.* **25**, p. 27 (1916).

anhydrous chlorides with calcium, barium, sodium, potassium, or ammonium halides is fused in an iron pot and subjected to electrolysis. If too much basic chloride is present, the metal and chloride emulsify and prevent the agglomeration of the metal. The misch metal collects in the bottom of the pot and is drawn off at intervals into molds. Prepared in this manner, the metal resembles iron in appearance and contains from 1 to 5 per cent iron, with small amounts of oxides and carbides. Its properties resemble those of cerium very closely. Its most interesting property is its pyrophoric nature — if scratched with a file bright sparks are given off. These may be due either to the formation of a superficial layer of a sub-oxide[1] or to the breaking off of small particles which are ignited by the heat of friction. The pyrophoric property is much increased by alloying with a hardening metal, such as iron, nickel, manganese, tin, zinc, cobalt, and other metals.

The most widely used pyrophoric alloys contain iron,[2] which produces the spark-giving property when present in quantities varying from 10 to 65 per cent. Auer metal, which contains 35 per cent iron and 65 per cent misch metal, gives especially brilliant sparks and is widely used for cigar lighters, gas lighters, etc. During the war much use was made of pyrophoric alloys for firing mines, signaling, making tracer bullets, and shells for night firing, etc. The friction of the air causes the alloy to ignite and the path of the projectile is easily observed. Very little misch metal is needed for gas lighters since it is estimated that 1 pound of Auer metal will make 1300–1800 "fire stones," each of which will give 2000–6000 ignitions. The war-time demand was very considerable, and after the seizure of the patents by the Alien Property Custodian and the issuing of permits to several firms production was considerable. No definite figures of production are available, but it is estimated that in 1919 between 2000 and 3000 pounds per month were made in the United States.[3] This estimate is doubtless conservative, because a single plant in December, 1918, was producing 100 pounds of misch metal daily and was installing additional equipment which would nearly double its capacity. The price of

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[1] Hirsch, *Chem. and Met.* **9** 1543 (1911).
[2] Hirsch, *Trans. Am. Electrochem. Soc.* **37** 359 (1920).
[3] H. C. Meyer, *Eng. and Min. Jour.* **109** 233 (1920).

the ferrocerium is the highest of all ferro-alloys. Under Austrian patents in 1917 the price was $25 per pound, but during the first half of 1919 it was from $15–$18 per pound, and later in the year it dropped to $14 per pound. Misch metal sold for from $7–$9 per pound.

The sudden elimination of the demand for military purposes stimulated the efforts to find other uses for misch metal. On account of its extreme activity, especially toward oxygen, it is found to be a powerful reducing agent, and as such it is used for the reduction of some of the more refractory oxides, such as those of zirconium, tantalum, and columbium. Its extensive use for this purpose would be largely controlled by cost. A small amount of the metal in powder form finds use as a component of flashlight powders, where it produces more intense action. Recently it has been applied as a scavenger for cast iron with exceedingly interesting results. Its usefulness for this purpose depends on the facts that its melting point is below that of iron and that its affinity for oxygen is great enough to remove oxidized particles, but its action is not so intense as to be difficult of control. Experiments have shown that the addition of small amounts of cerium remove oxygen thoroughly and increase the fluidity by keeping the metal hot for a longer period. As a result, the casting has a finer structure with more uniform distribution of graphite, greater soundness, and it machines much better. Misch metal melts at about 750° C. and is so active that much of it is lost in adding it to the molten iron. If the ferrocerium is used, its melting point is still below that of iron and its chemical activity is decreased so the loss is less. The alloy is best added in granular form by sprinkling it into the stream of metal as it flows into the ladle. The granulation of misch metal must be accomplished under a hydraulic press, as attempts to pulverize it with a hammer will probably ignite it. The amount needed to purify cast iron is small. As little as 0.05–0.10 per cent is sufficient if care and skill have been used in the preparation of the charge. If as much as 0.50 per cent is added, none of the cerium seems to remain in the casting. If larger amounts are used, some of the cerium remains in the iron as an alloy, but so far as is known it produces no beneficial results. Consequently, the cerium is added in very small amounts, causing only slight increase in cost.

The addition of 0.2 per cent misch metal to aluminium has a very beneficial effect as a purifying agent, greatly increasing the ductility of the metal.[1] The cerium is added by mixing its fluoride in the electrolytic bath while the aluminium is being prepared, or, better, misch metal is thoroughly incorporated with the molten aluminium. The alloys of aluminium with copper and magnesium also have increased ductility when cerium is added, but those with zinc do not appear to be influenced. This is an important consideration since these alloys normally possess low ductility.

The addition of cerium to brass is harmful, since it increases the number of leaky castings and lowers both tensile strength and ductility. Cerium forms many other alloys. Tin mixes with it in all proportions,[2] forming pyrophoric alloys up to 80 per cent tin. The hardest and most pyrophoric alloy contains 30 per cent tin, and those with low tin content are not very stable in the air.

Cerium and aluminium may be alloyed by heating the two metals together rapidly,[3] though there is some difficulty in obtaining a uniform product. The alloys richest in cerium are pyrophoric, the others are not; those containing not more than 25 per cent aluminium are slowly attacked by water and the atmosphere, but the ones containing more than 25 per cent aluminium are remarkably stable.

Magnesium alloys [4] readily with cerium, but uniformity is possible only by stirring or by repeating the fusion. The alloy containing equal molecular quantities of the metals has a hardness of 5, is strongly pyrophoric, burns violently on heating but is stable in the air at ordinary temperatures and is more resistant to acids than pure cerium. The alloys with magnesium are extremely brittle; those containing 60–75 per cent cerium are easily powdered and make excellent flashlight powders or reducing agents. Cerium alloys with both silicon and bismuth,[5] the union taking place at elevated temperatures with considerable vigor.

Sodium and cerium unite quietly and form a hard alloy which is somewhat pyrophoric. It oxidizes in the air.

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[1] *Metal. Ind.* **20** 142 (1922), translation from *Metall und Erz*, May 22 (1921).

[2] Vogel, *Zeit. anorg. Chem.* **72** 319(1912).

[3] Vogel, *ibid.* **79** 41 (1912–13).

[4] Vogel, *ibid.* **91** 277 (1915).

[5] Vogel, *ibid.* **84** 323 (1913–14).

Silver forms a hard, brittle alloy with cerium, but the gold alloy is fairly soft.

Copper alloys are unstable if they contain more than 30 per cent cerium. The alloys containing 55 per cent cerium or more are pyrophoric.

Calcium forms very hard white alloys with cerium. They are stable in the air and strongly pyrophoric.

Other pyrophoric alloys are prepared by mixing the misch metal with titanium, boron, cadmium, lead, manganese, antimony, mercury, etc. Stearn states that 200 tons of ceria are used annually in the manufacture of pyrophoric alloys.

Compounds of cerium and its relatives find numerous suggested uses. The pyrophoric metal known as "kunheim" is a mixture of the hydrides of the cerium earth metals with magnesium and aluminium. Cerium fluoride and titanofluoride have been used in the preparation of electrodes for the flaming arc light. By impregnating the carbon electrodes with the cerium salts a more intense light is obtained and the arc burns evenly and quietly. Stearn declares[1] that 300 tons of ceria are used annually for this purpose.

Cerium carbide and nitride have been tried as filaments for incandescent lamps.[2] Pure cerium nitrate is used in the manufacture of gas mantles. The reducing action of cerous compounds is used for producing a variegated effect in dyeing fabrics. The salts of cerium are used for making aniline black and as a base for the alizarin group of dyestuffs.

The oxides have been suggested for use with tin compounds for weighting silk. In dyeing leather cerium compounds are good mordants. In the manufacture of glass the cerium earths are used as coloring agents, one per cent producing a clear yellow and larger amounts producing brown. The fluoride, dioxide, and silicofluoride have been used in the preparation of enamels. Ceric titanate produces a shining yellow color in porcelain, while the molybdate produces a bright blue, the tungstate a bluish green, and manganese ceric titanate an orange yellow. In photography the sulfate is sometimes used for removing silver from an overdeveloped negative and in the preparation of color photographs. In medicine the mixed

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[1] Johnstone, *Jour. Soc. Chem. Ind.* **37** 373 (1918).

[2] *Elect. Eng.* **48** 416 (1908).

oxalates have been suggested as a remedy for seasickness, epilepsy, and hysteria. Cerium phenolate is a disinfectant which is as efficient as phenol and much less toxic.[1] "Ceriform" is an antiseptic which is composed of certain ceric double sulfates. The sulfates may be used as catalysts in the contact process for sulfuric acid, and the chlorides when heated to 350°–480° C. are efficient catalysts in the Deacon process for manufacturing chlorine. Cerium hydride and nitride catalyze the union of hydrogen and nitrogen in the direct manufacture of ammonia, but no method has yet been discovered for preventing the mass from losing its activity. Cerium sulfate is found to have certain advantages over lead as an accumulator in storage batteries. Ceric oxide is an active oxidizing agent useful in the manufacture of aldehydes, quinones, etc., from aromatic hydrocarbons. If these reactions are carried out in an electrolytic cell, the cerous sulfate formed by the reaction is immediately reoxidized, and the process becomes continuous. The oxidizing power of ceric oxide is also used in the combustion tube for ultimate organic analysis.[2]

None of these uses, however, seems destined to create any considerable demand for the cerium group compounds. There is no concern about the supply of cerium since all that is used at the present time may be considered as a by-product. If the demand should exceed this supply, much cerium could be extracted from minerals like allanite which are now not used.

Compounds. — Cerium forms two well defined series of salts in which it is trivalent and quadrivalent respectively. In its trivalent condition cerium is more basic than in its quadrivalent state, hence, the cerous salts are more stable, and more numerous. The cerous salts of colorless acids are white, while the ceric salts are yellow, orange, or red in color. Cerous salts are oxidized to ceric by lead peroxide or bismuth tetroxide in nitric acid solution; by ammonium persulfate or sodium bismuthate in sulfuric acid solution; by electrolysis of the nitrate or sulfate in a strongly acid solution; by sodium hypochlorite or by potassium permanganate in alkaline solution. Hydrogen peroxide in alkaline solution oxidizes cerous to ceric or perceric compounds. Because ceric chloride is so very unstable oxida-

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[1] *Ger. Pat.* 214, 782 (1909).

[2] Dennstedt method, Bekk. *Ber.* 46 2574 (1913).

tion to the ceric condition cannot be carried out in hydrochloric acid solution.

Ceric compounds are reduced to cerous very easily by such reagents as hydrogen peroxide in acid solution, sulfur dioxide, hydrochloric acid, oxalic acid, stannous chloride, ferrous sulfate, etc. The transformation of ceric oxide to a cerous salt requires the presence of the desired acid and a reducing agent, since CeO_2 is difficultly soluble in mineral acids. It may be accomplished by: (1) nitric acid and hydrogen peroxide; (2) hydroquinone and hydrochloric or sulfuric acids; (3) hydrochloric acid and an alkali iodide.

The cerous salts are derivatives of Ce_2O_3, which may be prepared by reducing CeO_2 with hydrogen at 2000° C. and 150 atmospheres pressure. Ignition of a cerous salt produces CeO_2, completely in the air and partially in hydrogen or in a vacuum. The cerous salts resemble those of lanthanum and yttrium very closely. For the characteristics of the individual compounds see pages 111–113.

The ceric salts are derivatives of CeO_2, which is feebly basic. As a consequence they are considerably hydrolyzed in solution and give an acid reaction. Normal ceric salts of weak acids are unknown, and even the chloride and nitrate are known only as double or complex salts. Reduction to cerous compounds is easily done in acid solution, but much more difficult to accomplish in alkaline media. Ceric compounds easily form colloidal solutions which do not appear to be basic salts of the ordinary type.

A few of the more important ceric compounds are included in the following summary.

Ceric oxide, CeO_2, is prepared by igniting cerium or any cerous or ceric salt of an oxy-acid. Its density depends upon the method of preparation. The color is the subject of much discussion.[1] We would expect a white oxide like zirconia and thoria. White oxides have been prepared, but Brauner has shown that such ceria contains impurities. As usually obtained ceria has a pale yellow color. It volatilizes without melting or decomposition at about 1900°. Besides being a weak base it shows slight evidence of faintly acidic properties. While pure ceria is insoluble in nitric or hydrochloric acids, a mixture of rare earth oxides dissolves readily

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[1] See Sterba, *Compt. rend.* **133** 221 (1901) and *Ann. Chim. Phys.* **2** (viii) 193 (1904); Wyrouboff and Verneuil, *ibid.* **9** 356 (viii) (1906); Meyer, *Zeit. anorg. Chem.* **37** 378 (1903); Brauner, *ibid.* **34** 207 (1903); Neish, *Jour. Am. Chem. Soc.* **31** 517 (1909); Spencer, *Trans. Chem. Soc.* **107** 1265 (1915).

provided the ceria does not exceed 45–50 per cent. The usual explanation of this peculiarity is that the ceric oxide is acidic to the more basic rare earth oxides and forms salts of the type $M_2O_3 \cdot 2\ CeO_2$ or $2\ M_2O_3 \cdot 3\ CeO_2$. Deep blue crystals of the composition $UO_2 \cdot 2\ CeO_2$ are obtained by igniting a mixture of cerous and uranyl sulfates or by precipitating an aqueous solution of uranyl and cerous nitrates with ammonia or dilute potassium hydroxide. The so-called cero-ceric oxide, formed by reducing CeO_2 with hydrogen at red heat, to which the formula Ce_4O_7 is usually given, may be a cerous cerate of the formula $Ce_2O_3 \cdot 2\ CeO_2$.

Ceric hydroxide, $Ce(OH)_4$, is not known. A hydrated oxide, probably $Ce_2O(OH)_6$, forms as a yellow gelatinous precipitate when ammonia or an alkali hydroxide is added to a ceric salt. It may also be prepared by the oxidation of cerous hydroxide. It dissolves in nitric acid, forming a ceric salt, in sulfuric acid yielding a partially reduced product, and in hydrochloric acid giving cerous chloride and chlorine.

Ceric nitrate, $Ce(NO_3)_4$, is not known as a simple salt, but double nitrates of the type $Ce(NO_3)_4 \cdot 2\ M'NO_3$ are formed with the alkali metals and ammonium. In aqueous solutions these salts are readily hydrolyzed, but they are the most stable ceric salts. The ammonium ceric nitrate is important in the purification of cerium. A series of double nitrates, $M'(NO_3)_2 \cdot Ce(NO_3)_4 \cdot 8\ H_2O$, is also formed, but they are less stable than the alkali double salts. When ceric hydroxide is evaporated with nitric acid, crystals of the basic salt $2\ CeOH(NO_3)_2 \cdot 9\ H_2O$ are obtained.

Ceric fluoride, $CeF_4 \cdot H_2O$, is probably the only ceric halogen compound known in the solid form. It is a brown powder insoluble in water, prepared by adding hydrogen fluoride to ceric hydroxide. It readily forms double fluorides with the alkali metals and copper, cadmium, cobalt, nickel, and manganese.

Ceric chloride, $CeCl_4$, is known only in solution. It is prepared by dissolving ceric hydroxide in concentrated HCl, but the evolution of chlorine begins at once and proceeds rapidly if the solution is hot. It forms double chlorides with organic bases, such as pyridine, quinoline, and triethylamine.

Basic ceric carbonates of varying composition are formed as a yellow gelatinous precipitate when an alkali carbonate is added to the solution of a ceric salt. Perceric potassium carbonate, $4\ K_2CO_3 \cdot Ce_2(CO_3)_3O_4 \cdot 12\ H_2O$, is prepared by adding hydrogen peroxide to a mixture of ceric and potassium carbonates. If more H_2O_2 is added, all the cerium is precipitated as an orange yellow precipitate.

Ceric sulfate, $Ce_2(SO_4)_3$, is prepared in the anhydrous condition when CeO_2 is heated on a sand bath with H_2SO_4. It is a deep yellow crystalline powder, soluble in water, somewhat hydrolyzed and on dilution or boiling a basic sulfate is formed. When heated in the air the normal sulfate begins to lose weight at 155°, and at 300° it loses all its sulfur trioxide.

Detection. — Very small quantities of cerium may be detected by adding the neutral solution to warm concentrated potassium carbonate solution and then adding a few drops of dilute hydrogen peroxide. A yellow color indicates cerium.

If a neutral solution of a cerous salt is added to an ammoniacal silver nitrate solution, the coloration varies from brown to black, depending on the amount of cerium present.

An ammoniacal solution of cerous tartrate is oxidized by air or H_2O_2, forming a yellowish brown color.

When NaClO is added to a colorless cerous solution red ceric hydroxide is precipitated; this dissolves in warm HCl, with the evolution of chlorine.

Cerium may be detected if present to the extent of 0.112 mg. per liter[1] by the following test: make the solution to be tested slightly alkaline, boil, and filter a portion of the precipitate; sprinkle on the filter an acetic acid solution of benzidine. A bright blue coloration indicates cerium, if oxidizing agents, especially those of manganese, cobalt, thallium, and chromium, are absent. Cerium fluoride, carbonate, and bisulfate do not respond to the test.

Cerous salts show no absorption lines, but ceric salts show a general absorption toward the violet end of the spectrum. The spark spectrum contains a number of bright lines, especially in the green and blue.

Estimation. In the absence of rare earth metals cerium may be precipitated as the hydroxide or oxalate and ignited and weighed as CeO_2.

Several volumetric methods are available: (1) in Bunsen's method the oxide is dissolved in HCl in the presence of KI, and the liberated iodine being estimated with $Na_2S_2O_3$ or H_3AsO_3. This method does not give very satisfactory results since the other rare earth oxides in the presence of CeO_2 will also liberate iodine. (2) Ceric sulfate is reduced by H_2O_2 and the excess peroxide determined by permanganate. The cerous salt reduces the permanganate slowly so the titration is finished without delay and the first end point taken. (3) Ceric salts may be reduced by ferrous sulfate and the excess estimated by permanganate. (4) Cerous salts may be oxidized by potassium ferricyanide in alkaline solution, the precipitate filtered off and the ferrocyanide formed titrated with permanganate in acid solution. (5) Cerium oxalate may be dissolved in sulfuric acid and the liberated oxalic acid titrated with permanganate.

Any method depending on the oxidation of cerous salts to ceric in alkaline solution by permanganate requires special care because of the oxidation of cerous hydroxide by the air.

THORIUM

Historical. — In 1817 Berzelius found what he supposed to be a new earth in the mineral gadolinite and suggested for it the name "thoria" from Thor, son of Odin, Scandinavian god of war. In 1824 he became convinced that this new earth was a basic phosphate of yttrium. In 1828 he was examining the mineral now known as thorite and discovered a new earth with properties suggestive of the former thoria. So he transferred the name and showed the resemblance to zirconia. In 1851 Bergmann announced the discovery of a new element called donarium from the mineral orangite; in 1862 Bahr discovered wasium, but both these elements have been shown to be identical with thorium.

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[1] *Jour. Soc. Chem. Ind.* **39** 16 A (1920).

The homogeneity of the element has been questioned several times. The most notable case was in 1901, when Baskerville announced that by the fractional distillation of thorium chloride he had isolated two new elements, berzelium and carolinium. His conclusion has not been confirmed[1] and thorium is now regarded as a distinct chemical element, isotopic with ionium, radiothorium, etc. No particular attention was paid to the element until Auer von Welsbach devised the incandescent gas mantle in 1885. At that time the only sources of thorium known were the rare earth minerals, which were too rare to supply any considerable commercial demand. A geological survey was conducted, however, and extensive deposits of monazite sand became available.

Occurrence. — Thorium forms a rare silicate, known as thorite, which resembles zircon closely. It is usually a black hydrated mineral, but is sometimes clear with an orange-yellow color, when it is known as the gem orangite. It contains about 60 per cent thoria associated with the silicates of uranium,[2] iron, manganese, copper, magnesium, lead, tin, aluminium, sodium, and potassium. Thorianite is another rare mineral which contains about 80 per cent thoria, associated with the oxides of the rare earth metals and uranium. It is found chiefly in Ceylon, where the mineral was discovered in 1904. The following year nine tons of this mineral were produced, but the supply is uncertain, and so it is not an important source of thorium. The thoria is easily extracted, however, and when thoranite is available it commands a high price. In 1905 it sold at prices up to £1700 per ton. Thorium also occurs in varying quantities in most of the rare earth minerals, especially monazite, gadolinite, euxenite, and samarskite. It is found in traces in many of the common minerals, and in many igneous and sedimentary rocks.

The principal supply of thoria is obtained from monazite sands, which are found in Brazil, India, the Carolinas, Idaho,[3] and in many other localities. Monazite is essentially a phosphate of the cerium earths which contains varying amounts of thorium as an accessory constituent. Originally it is a constituent in pegmatites, granites, and gneisses, in which it occurs

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[1] See Baskerville, *Jour. Am. Chem. Soc.* **23** 761 (1901); **26** 922 (1904); *Ber.* **38** 1444 (1905); Brauner, *Proc. Chem. Soc.* **17** 67 (1901); Meyer and Gumperz, *Ber.* **38** 817 (1905); Eberhard, *ibid.* 826.

[2] For a study of the Th:U content of minerals see Meyer, *Sitzb. Akad. Wiss. Wien.* **128** (2*a*) 897 (1919); C. A. **15** 1853 (1921).

[3] See U. S. Geol. Surv. *Min. Resources* for 1909, *p.* 898; U. S. Geol. Surv. *Bull.* 430 (1910).

in too small quantities for commercial use. The weathering of these rocks has been followed by the water concentration, so that the only commercial deposits are along the river beds or upon the beaches, where it is associated with other heavy minerals.

The deposits in Brazil are on the seashore and along the river bottoms of the interior. The latter are expensive to work on account of the low monazite content (about 0.3 per cent) and the difficulties of transportation. The beach sands have accordingly supplied most of the material which has been exported. For many years these deposits supplied a very large part of the world's thoria.

The deposits in India are chiefly on the seacoast of Travancore. They cover a known area of 1427 acres, and in some places the deposit is nearly 20 feet deep. The monazite in sight was originally estimated at 1,776,000 tons, but recent surveys indicate that this estimate is much too small. The per cent of thoria is nearly double that of the Brazil mineral (see Table XXVI, page 169), and since labor is very cheap, the cost of production is low.

The Carolina deposits are along the river beds and are covered by about 4 feet of earth. The deposits vary from 1 to 10 feet in thickness.[1] For several years considerable monazite was obtained from these deposits, but the difficulty of mining, the low thoria content, and keen competition has almost wholly eliminated the American supply from the world's market. Efforts have recently been made to develop the deposit at Pablo Beach, Florida.

In prospecting for monazite it is customary to concentrate the sand by panning as in a search for gold. The monazite is heavy and has a yellow or brown color (rarely almost black) and a peculiar luster. The presence of certain rare earth elements makes accurate field diagnosis possible by the use of a hand spectroscope. If the concentrated sand is spread out on a piece of paper or a cloth and examined by the spectroscope with natural light falling directly on the sand, a broad line is observed between the yellow and red and a narrower line in the green. These absorption lines are probably due to the presence of neodymium and erbium.

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[1] See J. H. Pratt, *Economic Paper*, No. 14, N. Carolina Geol. Surv.

The mining of monazite is accomplished by open mines, usually of the simplest sort. The first steps in purification are taken before shipment is made, and they depend on washing out the lighter grains of silica, magnetite, ilmenite, zircon, and garnet and leaving the heavier monazite behind. Such methods of concentration are wasteful, but pretty satisfactory results are obtained by sizing the gravel before sluicing. More refined methods of concentration are now generally used, such as the shaking tables of the Wilfley type, used in Brazil, and dry blowing, used in India. The final and most efficient means of concentration is by the use of electromagnetic separators. These separate the other minerals from monazite and to some extent from each other by means of the differences in magnetic permeability. As usually carried out the partially refined monazite is dried and carefully sized and subjected to electromagnets of increasing intensity. These remove in order (1) magnetite, (2) hematite and ilmenite, (3) garnet, platinum, epidote, apatite, olivine, and tourmaline, (4) coarse monazite with small amounts of zircon, rutile, epidote, etc., (5) fine monazite. The non-magnetic residues, containing gold, zircon, rutile, quartz, feldspar, etc., may be separated by means of an oscillating table.

Attempts have been made to utilize the by-products but without marked success. The ilmenite finds difficulty in competing with the native ore. The garnets are small, with rounded corners, and so of no value as abrasives. A small quantity of garnet of larger particles has been broken and used as abrasive. The gold has been recovered at a profit even when present in so small an amount as 1½ cents per ton of the original gravel.

The world's consumption of monazite is estimated at about 3000 tons per year. Three-fourths of the world's supply of monazite in 1915 came from India, and since this ore contains a higher per cent of thoria, this corresponds to 90 per cent of the thorium production. This is used for its thorium content, which determines the price of the mineral. During 1920 monazite sand with a guaranteed minimum of 6 per cent ThO_2 ranged in price from \$25 to \$30 per unit,[1] duty paid. Thorium nitrate sold wholesale for \$3.75 to \$4 per pound.

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[1] A unit means one per cent per ton. Thus, six per cent sand at \$27 per unit would cost \$162 per ton.

TABLE XXVII

World's Production of Monazite Sand in Metric Tons

	BRAZIL	UNITED STATES	INDIA	CEYLON
1909	6,359	242	None	—
1910	5,345	44.3	None	—
1911	3,627	1.6	819	—
1912	3,344	0.6	1,135	—
1913	1,415	None	1,234	—
1914	599	None	1,185	—
1915	439	16.1	1,108	—
1916	None	16.5	1,292	—
1917	1,136	34.7	1,940	—
1918	499	No data	2,117	20
1919	146	No data	2,023	40
1920	1,153	No data	1,667	70
1921	—	No data	Ca 1,600	Ca 70

From monazite residues mesothorium is extracted, and a small amount of misch metal is prepared.

Extraction. — From thorite and thorianite the extraction of thoria is easily accomplished. The minerals are easily dissolved in hydrochloric or sulfuric acid (nitric acid may be used for thorianite) and the solution evaporated to expel excess acid and dehydrate the silica. The residue is extracted with water, and the solution saturated with hydrogen sulfide to remove heavy metals. Separation from the rare earth metals may be accomplished by the carbonate, sulfate, or oxalate methods.

From monazite the extraction is difficult because of the small amount of thoria and the large quantities of elements with similar properties. Many methods are available in the laboratory which would be too expensive for factory use. The methods actually used are carefully guarded secrets and doubtless differ in accordance with the type of ore used. The following may be considered as typical. The ore is ground, if it contains large grains, and added gradually to twice its weight of hot concentrated sulfuric acid in cast iron pans. Heating is continued until the monazite grains have entirely disappeared. Then the mass is poured slowly into cold water, and silica, rutile, zircon, etc., filtered out. The solution contains sufficient acid to prevent the precipitation of the sparingly soluble earth phosphates. If ammonia or magnesia is added, or if the solution is largely diluted, the thorium phosphate is precipitated since it is more sparingly soluble than the rare earth phosphates. The removal of the phosphoric acid may be accomplished by dissolving the mixed phosphates in HCl and precipitating thorium oxalate with oxalic acid. A less expensive method is to digest the phosphate with soda ash and precipitate $Th(OH)_4$ with sodium hydroxide. The phosphorus must be completely removed since phosphates cause the mantles to be exceedingly brittle. Not more than 0.0004 per cent of P_2O_5 is generally permitted.

From the sulfuric acid solution, thorium may also be obtained by precipitation with sodium fluosilicate, sodium hypophosphate,[1] or sodium pyrophosphate.[2] An ingenious method for removing the phosphorus has been proposed by Baskerville[3] and used on a large scale. It consists in heating in an electric furnace a mixture of monazite, coke, lime, and feldspar. The phosphorus is distilled out and the mass allowed to cool. When extracted with water, acetylene is evolved from the calcium carbide formed during the heating, and the remainder crumbles to a fine powder. This is dissolved in hydrochloric acid, and the cerium earths removed.

Separation. — The separation of thorium from the rare earth metals with which it is still mixed may be accomplished by three methods: (1) the carbonate separation depends on the fact that thorium carbonate is much more soluble in sodium carbonate than the carbonates of the rare earth metals; (2) by the fractional crystallization of the mixed sulfates at 15°–20°, crystals of $Th(SO_4)_2 \cdot 8\,H_2O$ are obtained at the insoluble end of the series; (3) thorium oxalate forms a soluble double salt with ammonium oxalate, while the rare earth oxalates are almost insoluble in this reagent. Some other methods which have been suggested are fractionation of the chromates,[4] of the hydrogen alkyl sulfates,[5] of the acetates, by the use of sebacic acid[6] and hydrogen peroxide.

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[1] See Rosenheim, *Chem. Ztg.* **36** 821 (1912); Wirth, *Zeit. angew. Chem.* **25** 1678 (1912); Koss, *Chem. Ztg.* **36** 686 (1912).

[2] Carney and Campbell, *Jour. Am. Chem. Soc.* **36** 1134 (1914).

[3] Eighth International Congress of Applied Chem. **2** 17 (1912).

[4] Muthmann and Baur, *Ber.* **33** 1756, 2028 (1900).

[5] *Ger. Pat.* 233,023 (1911).

[6] *Ger. Pat.* 266,459 (1912).

For the manufacture of gas mantles very pure thorium nitrate is required, since the presence of more than very slight traces of other oxides greatly reduces the candle power of the light. As an indication of the efficiency of the extraction and purification methods it is worthy of note that between 80 and 90 per cent of the thoria present in the monazite is obtained in the form of the nitrate of sufficient purity for mantle manufacture.

Considerable thorium nitrate is obtained from factory trimmings and worn-out mantles. Usually this material is pulverized, sieved, dissolved in sulfuric acid, converted to the nitrate and used again in making up the lighting fluids.

Metallurgy. — The high melting point of thorium, its chemical activity toward hydrogen, oxygen, nitrogen, and carbon, and its fondness for alloying with metals make its metallurgy particularly difficult. The metal has not yet been obtained in a pure state.

Berzelius attempted in 1829 to reduce the double chloride, $2\,KCl \cdot ThCl_4$, with sodium or potassium, but failed to get complete reduction. Magnesium only partially reduces ThO_2, while silicon yields a silicide, carbon gives a carbide, and aluminium produces an alloy. By electrolysis an impure metal is obtained which always contains oxide and other impurities. Probably the best results have been obtained by reducing carefully prepared anhydrous thorium chloride with sodium in a sealed tube. By this method Moissan and Hönigschmidt[1] prepared the metal which contained only 3 per cent of the oxide, and von Bolton[2] obtained a product which he claims was free from oxide. Thorium has also been produced by passing sodium vapor with such volatile thorium compounds as the acetylacetonate through a red-hot tube.[3]

Properties. — As ordinarily prepared, thorium is a dark gray powder consisting of shining microscopic plates. It may be hammered or rolled into the coherent form, when it resembles platinum in appearance, hardness, and ductility. The powder has a density of 11.0–11.3, and the coherent metal of 12.16. The metal is magnetic, having a susceptibility of $+0.18 \times 10^{-6}$,

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[1] *Ann. chim. Phys.* 8 (viii) 182 (1906).
[2] *Zeit. Elektrochem.* 14 768 (1908).
[3] Siemens and Halske, *Ger. Pat.* 133,959 (1900).

its value rising rapidly with increased temperature to 400°. According to von Bolton the melting point is 1450°. The specific heat is 0.02787 at ordinary temperatures. The fine powder ignites when rubbed or crushed in the air and the ribbon burns brilliantly just below red heat, giving off a shower of sparks and forming the oxide. Its heat of combustion is 326,000 calories. At a temperature around 450° it burns brilliantly in chlorine, bromine, iodine, and sulfur; at about 650° it combines directly with either hydrogen or nitrogen. Concentrated hydrochloric acid and aqua regia dissolve the metal rapidly, but sulfuric, hydrofluoric, and dilute hydrochloric acids attack it slowly. When first immersed in nitric acid it is dissolved very rapidly, but the metal is soon rendered passive and the action stops. The alkalies do not attack it. It is slightly more electropositive than magnesium, and alloys readily with such metals as aluminium, copper, nickel, zirconium, and tungsten.

Thorium is strongly radioactive.

Uses. — Alloys of tungsten and thorium are used for making the filaments of incandescent electric lamps. When tungsten alone is used, much difficulty is encountered because after short use the metal becomes crystalline and vaporizes, resulting in blackening of the bulb. The filament becomes hard and brittle and frequently breaks. This tendency to crystallize may largely be overcome by alloying tungsten with thorium and other rare earth metals. Sometimes tungstic oxide is mixed with 1-4 per cent thoria,[1] pressed into rods, and reduced by hydrogen at red heat. Another process mixes 7 per cent thorium tungstate with finely divided metallic tungsten and an organic binding material[2] and produces the filament by a squirting process. Filaments are also made by mixing colloidal tungsten with thorium. These alloy filaments are said to be exceedingly ductile, even in the cold, and have the ability to resist crystallization during long use. The function of the thorium in these filaments has not as yet been definitely established. It is possible that ThO_2 forms a solid solution with the tungsten.[3]

An alloy consisting of tungsten containing from 0.5 to 10 per cent of thorium is used as the cathode of an electrical discharge apparatus devised by Langmuir. It is said to give an

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[1] *Eng. Pats.* 5026 and 8758 (1912).

[2] *French Pat.* 447,584.

[3] E. Wedekind, *Edel Erden und Erze*, **3** 109 (1922).

electron emission at 1300°–1380° A. which is equal to that given by pure tungsten electrode at 2000° A.

Thorium salts have a bactericidal and antitoxic action, as is shown by experiments with guinea pigs. Ten pigs which had received twice the lethal dose of cholera survived when treated with thorium or lanthanum salts, while the control pigs not so treated died within 30–36 hours.[1] A solution containing 0.5–1.0 gram of thorium sulfate per liter is as toxic to lower organisms and ferments as mercuric chloride.[2]

The compounds of thorium find extensive use on account of their radioactive nature.

Thoria has been used successfully as a catalyst in the synthesis of many organic compounds. Thus both symmetrical and unsymmetrical ketones may be prepared directly from monocarboxylic acids;[3] alcohols are converted into ethers or olefines according to the temperature employed; benzyl alcohol forms esters with formic, acetic, propionic, isobutyric, and benzoic acids; and ammonia and alcohols passed over thoria at 360° yield olefines and primary amines.[4]

Small pencils of thoria containing about 1 per cent of ceria become brilliantly incandescent when heated to a moderate temperature. Such lamps are finding considerable use wherever the electric current is not available, for searchlights, automobile headlights, and projection lanterns for moving pictures.

Numerous patents[5] have been issued for the use of thorium chromate, thorium tungstate, and other salts in the preparation of magnesium flashlight powders. It is claimed that such powders evolve less smoke than those which consist of magnesium alone.

The only important commercial use of thorium, however, is in the manufacture of incandescent gas mantles. This industry had a very modest beginning in 1884 when Welsbach patented the use of a fibrous network of rare earth oxides which were to be heated by an ordinary gas flame of the Bunsen type. The first mantles were composed of a mixture of zirconia, lanthana,

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[1] *Compt. rend.* **159** 410 (1914).

[2] *Ibid.* **143** 690 (1906).

[3] Senderens, *ibid.* **148** 927 (1909); Koehler, *Bull. Soc. Chim.* **15** 647 (1914).

[4] Maile, *Chem. Zeit.* **34** 1173 (1911).

[5] *French Pats.* 14,692 (1908) and 403,722 (1909); *Eng. Pat.* 27,267 (1904).

and yttria. These were not successful because they were very fragile and possessed low powers of illumination. In 1886 thoria alone or with a small per cent of rare earth oxides gave better results, but not until 1893 can it be said that actual success was assured. In this year a patent was issued for the use of 99 per cent thoria and 1 per cent ceria. This gave a mantle which was strong and became brilliantly luminous at relatively low temperatures. No other arrangement has yet been discovered which produces so satisfactory results. If the amount of ceria is either increased or decreased, the luminosity decreases rapidly. See Fig. 11. It is probable that the ceria is held in solid solution [1] by the thoria.

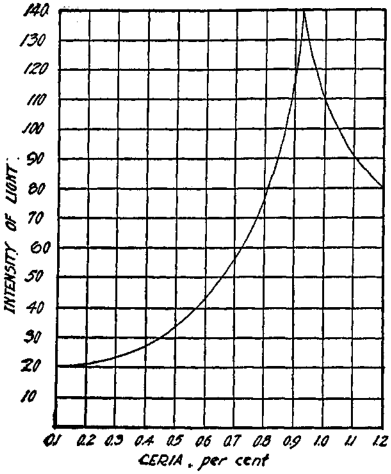

FIG. 11.—EFFECT OF COMPOSITION ON THE INTENSITY OF LIGHT EMITTED BY MIXTURES OF CERIA AND THORIA.

The importance of this industry is seen in the statement that the world's annual consumption of incandescent mantles is about 300,000,000,[2] of which the United States consumes about 80,000,000. Since each mantle contains about 0.5 gram of thoria representing 1 gram of the nitrate, the world's total consumption of the nitrate will be 300,000 kilograms. Previous to the outbreak of the war the industry was almost absolutely controlled by German and Austrian interests. English and French mantle manufacturers depended on German and Austrian supplies of thorium nitrate. With the outbreak of the war this supply was cut off. Soon there developed a vastly increased demand for gas mantles on account of the "stripping" of the gas supplies of those constituents which give luminosity to the gas, in order to obtain material for the manufacture of high explosives. The stripped gas still possessed

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[1] White and Travers, *Jour. Soc. Chem. Ind.* **21** 1012 (1902).

[2] Estimate of Karl L. Kithil, Bur. of Mines, *Tech. Paper* 110, p. 9.

splendid heating power and could be used efficiently for lighting if the burner were provided with an incandescent mantle. To meet these increased needs European manufacturers turned to American sources of thorium nitrate. As a result several new producers entered the market and production increased enormously. See Table XXVIII. Thirty or more producers[1] are said to be engaged in the manufacture of mantles in the United States and the exports now exceed the pre-war imports. Competition has been keen enough to keep prices down and quality up.

TABLE XXVIII

Principal Imports of Thorium Material into the United States

	MONAZITE (AND THORITE)		THORIUM NITRATE	
	Pounds	Value per Pound	Pounds	Value per Pound
1913	1,145,010	$0.082	112,105	$1.89
1914	770,840	0.080	101,927	2.35
1915	1,873,971	0.117	67,406	2.52
1916	1,221,399	0.098	909	4.27
1917	4,598,926	0.065	1,188	1.98
1918	2,994,515	0.068	None	—
1919	632,568	0.077	3,307	1.59
1920	1,814,182	0.078	35,640	1.21
1921	542,130	0.047	44,554	2.01

The manufacture[2] of incandescent mantles is based upon the impregnation of a combustible fabric with the nitrates of thorium and cerium and the ignition of this material by which the fabric is consumed and the nitrates converted to the oxides. The fabric selected was first long fiber cotton, which is still extensively used in the United States. Better grades of mantles are produced by the use of ramie, which before the war was used for the production of 90 per cent of the mantles made in Europe. Artificial silk has been used with very satisfactory results, as it gives a mantle which is strong and elastic, and

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[1] U. S. Tariff Commission, *Information Series*, No. 14 (1920).

[2] The process described is for mantles made of cotton or ramie. For more extended account see Johnstone, *Rare Earth Industry*, p. 15; Levy, *Rare Earths*, p. 265; Böhm, *Das Gasglühlicht* (1905) and *Chem. Ind.* **29** 450 (1906). For artificial silk mantles see Wirth, *Chem. Zeit.* **35** 752 (1911).

possesses high illuminating power, which it retains well. Artificial silk fabric has the advantage that it may be prepared in very pure form, thus making the long washing process unnecessary. The fiber is woven into a long tube or "stocking," various stitches being used and the tension of knitting depending on the purpose for which the mantle is to be used. The fabrics before impregnation must be free from fatty substances and nearly free from mineral matter. To this end the cotton fabric is washed first in dilute caustic soda, then in dilute hydrochloric acid; while ramie is soaked in dilute nitric acid, washed in water, then soaked in ammonia. The fiber as finally used should yield between 0.02 and 0.01 per cent ash. If the ash excedes 0.02 per cent, the mantle becomes brittle, especially if silica is present.[1]

After washing, the mantle fabric is thoroughly dried, then impregnated by soaking in the "lighting fluid." This is a solution containing 25–50 per cent thorium and cerium nitrates mixed in proportion to yield 99 per cent thoria and 1 per cent ceria. Occasionally beryllium nitrate, magnesium nitrate, or other salts are added to increase the strength of the ash. Inverted mantles sometimes have 0.5 to 0.8 per cent ceria. After impregnation the excess liquid is removed by a wringer or a centrifugal machine and the material carefully dried.

The asbestos loop and other supports are attached, and a process called fixing is sometimes employed, especially for mantles which are designed to withstand shock. This is accomplished by applying to certain parts of the mantle a solution which may contain borax, or nitrates of aluminium and magnesium. When the mantle is finished those parts which have been treated in this fashion are found to have a denser and stronger oxide, because of the greater shrinkage during the burning process. In this manner those portions of the mantle which are exposed to the greatest strain are reinforced.

Branding is accomplished by stamping a design upon the mantle fabric with a rubber stamp, wet with a solution the main constituent of which is "didymium" nitrate. This on ignition yields a colored oxide.

The mantle is next shaped on a wooden model and burned off, beginning at the top with a low temperature flame and finishing

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[1] *Jour. Soc. Chem. Ind.* **41** 2841 T (1922).

with a blast lamp. When first formed, the oxides which make up the mantle are soft and shapeless, but on ignition at the higher temperature the oxides become much more dense and rigid. The burning off was formerly done by hand, but now it is generally done by machine. During the burning off process there is considerable shrinkage, the amount of which depends upon the fiber, the particular stitch used, the tension of knitting, the amount of impregnating fluid, the ratio of ceria to thoria, and other factors. When thorium nitrate is ignited to the oxide it expands at least tenfold, but cerium oxide has essentially the same volume as the nitrate crystals from which it is prepared. Accordingly, the ratio of ceria to thoria by volume in the usual mantle is approximately 1 to 999.

After the hardening process the mantles are in exactly the same condition as when they are in use upon a burner. But in order to protect them against the shocks of transportation they are dipped into a collodion solution to which is sometimes added nitrates of thorium, zirconium, or beryllium for the added protection which these salts supply. After drying, the mantles are trimmed and packed for shipment.

The number of mantles manufactured from a pound of thorium nitrate varies widely with the size and quality of the mantles. In the United States about 325 is the average number produced from a pound of thorium nitrate, while in England the number varies from 225 to 450. As many as 600 of the cheaper German mantles are said to be prepared from a pound of the nitrate.

Compounds. — In its chemical relations thorium resembles both zirconium and quadrivalent cerium. It is somewhat more markedly electropositive than either of these elements, acidic properties being entirely absent. Its neutral salts are hydrolyzed somewhat in solution, and consequently are acid to indicators. They are however sufficiently stable to permit recrystallization from water solution. In basicity thorium approaches the elements of the yttrium group. Double salts are less common than with cerium and zirconium, but characteristic double nitrates, $R_2'Th(NO_3)_6$, crystallize well and are isomorphous with the analogous ceric double nitrates. Thorium resembles cerium in forming a double potassium sulfate which is insoluble in potassium sulfate solution, but differs from it in forming a double ammonium oxalate which is soluble in excess of ammonium oxalate.

The salts of thorium with colorless acids are colorless. In all its compounds thorium is quadrivalent.

Hydrogen unites directly with thorium at red heat, forming ThH_4, a stable powder, gray to black in color, unaffected by water but dissolved by HCl, yielding hydrogen. The formation of a gaseous hydride by action of dilute acids on an alloy of magnesium and thorium has been affirmed[1] and denied.[2]

Oxygen forms ThO_2, the most important oxide, and a peroxide, Th_2O_7 or ThO_3. The dioxide is prepared by igniting the hydroxide or the salt of an oxy-acid. It is a white powder whose properties depend on the source and temperature of formation. The nitrate yields a light voluminous powder, the sulfate gives a much more dense product. When fused with borax it yields tetragonal crystals isomorphous with rutile and cassiterite. When pure thoria is heated it glows very little, but when mixed with a small per cent of other oxides, especially ceria, it becomes brilliantly incandescent. It is difficultly soluble in acids, especially after ignition at high temperatures. If the oxide is suspended in concentrated sulfuric acid and the mixture evaporated, it is transformed into the sulfate. Fusion with $KHSO_4$ accomplishes the same result, but it is not attacked by an alkali carbonate fusion. It exists in an isomeric form, somewhat similar to that shown by zirconia and stannic oxide. The isomeric form is obtained as a gel, soluble in water, by repeated evaporation with small quantities of acid. It is sometimes called thorium meta-oxide and was formerly assigned the formula Th_3O_6. It is now generally considered as possessing the same formula as ordinary thoria.[3]

The peroxide is obtained as hydrated Th_2O_7 when ammonia and hydrogen peroxide are added to the solution of a thorium salt. It is unstable and loses oxygen readily, forming the relatively stable ThO_3. This is a very useful means of detecting and estimating thorium, by which it may be distinguished from both zirconium and the rare earths.

The hydroxide, $Th(OH)_4$, is precipitated as a gelatinous white mass when an alkali hydroxide or ammonia is added to solutions of a thorium salt. It is readily soluble in acids, forming salts, and in solutions of alkali carbonates, forming complex carbonates. It is not soluble in the alkalies, hence thorates are unknown. It is easily obtained as a positively charged colloid from which small quantities of electrolytes precipitate it.

Nitrogen unites directly with thorium, forming Th_3N_4. This compound may be prepared also by heating a mixture of ThO_2 and magnesium or aluminium in nitrogen or the carbide in ammonia. It is a dark red powder slowly decomposed by cold water and quickly by hot, forming ammonia and ThO_2.

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[1] Klauber and v. Mellenheim, *Zeit. anorg. allgem. Chem.* **113** 306 (1920).
[2] Schwarz and Konrad, *Ber.* **54 B** 2122 (1921).
[3] Stevens, *Zeit. anorg. Chem.* **27** 41 (1901).

The nitrate, $Th(NO_3)_4 \cdot 12\ H_2O$, is obtained by dissolving the oxide or carbonate in dilute nitric acid and allowing the solution to evaporate at room temperature. On heating the solution a hexahydrate is obtained, and if a considerable excess of nitric acid is present a pentahydrate forms. A dihydrate is also known. The commercial thorium nitrate is not a definite hydrate, but contains a quantity of water equivalent to a tetrahydrate. If the pure salt is ignited, a dense and harsh oxide results; but, if there is present 1 or 2 per cent of sulfuric acid the oxide is soft and bulky, occupying 6–10 times the volume of the nitrate. The voluminous ash is usually prepared for mantle manufacture. It forms a large number of double salts, like $2\,M'NO_3 \cdot Th(NO_3)_4$ with the alkali metals and $M''(NO_3)_2 \cdot Th(NO_3)_4 \cdot 8\ H_2O$ with nickel, cobalt, magnesium, zinc, and manganese. It also forms addition products with pyridine, quinoline, diethylamine, etc.

Phosphates of thorium are numerous. The normal phosphate, $Th_3(PO_4)_4 \cdot 4\ H_2O$, is precipitated as a bulky white mass by sodium phosphate. The precipitate always contains sodium. Thorium phosphate is more difficultly soluble in dilute acids than the other phosphates of monazite, consequently a partial separation of thorium is effected by means of sulfuric acid. A pyrophosphate, $ThP_2O_7 \cdot 2\ H_2O$, is precipitated by sodium pyrophosphate, and the meta-phosphate, $Th(PO_3)_4$, is formed by fusing $ThCl_4$ and HPO_3. Double phosphates are formed by fusing ThO_2 or $Th_3(PO_4)_4$ with the alkali phosphates; and mixed halogen phosphates, like $3\,ThO_2 \cdot ThCl_4 \cdot 2\ P_2O_5$, are prepared by heating the halide and metaphosphate.

Fluorine forms anhydrous ThF_4 as a fine white powder when hydrogen fluoride vapor is passed over $ThCl_4$ or $ThBr_4$ at 350°–400°. When HF is added to the solution of a thorium salt $ThF_4 \cdot 8\ H_2O$ is precipitated, but on drying in the air $ThF_4 \cdot 4\ H_2O$ forms. Thorium fluoride is insoluble in excess of HF, which permits the quantitative separation of thorium and zirconium. On igniting a hydrated thorium fluoride the oxide remains. Thorium fluoride forms double salts with the alkali fluorides, such as $K_2ThF_6 \cdot 4\ H_2O$, $KTh_2F_9 \cdot 6\ H_2O$, $KThF_5 \cdot H_2O$. These salts differ from the other double fluorides of Group IV by being amorphous and very sparingly soluble.

Chlorine forms $ThCl_4$ in a number of ways in all of which oxygen and moisture must be absent to prevent the partial formation of the oxychloride: (1) a pure salt is prepared by heating ThO_2 in a stream of chlorine and sulfur monochloride; (2) a mixture of the metal and its carbide, obtained by heating ThO_2 with C in an electric furnace, yields the chloride when heated in a stream of chlorine; (3) phosgene reacts with ThO_2, giving $ThCl_4$ and CO_2; (4) $ThOCl_2$ at red heat gives ThO_2 and $ThCl_4$. The anhydrous chloride forms colorless crystals which sublime at 720°–750°. They are deliquescent and dissolve readily in water with the evolution of much heat. The hydrate $ThCl_4 \cdot 8\ H_2O$ forms on crystallization; these yield a heptahydrate on drying at ordinary temperatures, a tetrahydrate at 50° and $ThCl_4 \cdot 2\ H_2O$ at 100°. Above this temperature basic chlorides are formed. Anhydrous thorium chloride combines directly with ammonia to form many addition compounds, some of which are decomposed by water and some are not. It also forms addition compounds with methylamine, ethylamine, propylamine, toluidine, pyridine, and quinoline; with alcohol, acetaldehyde, cinnamic aldehyde, acetone, salicylaldehyde. It forms double salts with the alkali chlorides, although such compounds are less numerous than in the case of the trivalent earths.

ThOCl$_2$ is formed when hydrated thorium chloride is heated to 250°. It is also formed when carbon tetrachloride begins to act upon hot ThO$_2$. It is very hygroscopic and dissolves in water without decomposition.

Bromine and iodine form compounds similar to the chlorine derivatives.

Th(IO$_3$)$_4$ is of considerable importance in the detection and estimation of thorium because in the presence of a large excess of alkali iodate it is insoluble in strong nitric acid while the rare earth salts dissolve readily.

Carbon forms ThC$_2$ when ThO$_2$ and carbon are heated in the electric furnace. It burns brilliantly in air, forming ThO$_2$, and in sulfur, giving a sulfide. Concentrated acids have little action upon it, dilute acids and water react more readily, producing a very complex mixture of gases which includes 47–48 per cent acetylene, 27–31 per cent methane, about 5 per cent ethylene, 16–18 per cent hydrogen, and small amounts of ethane, propane, butane, propylene, and some higher members of the acetylene series.

Carbonates are numerous, although they are mostly double or basic salts. When an alkali carbonate is added to the solution of a basic salt there is precipitated a basic carbonate, soluble in excess of the precipitant. The solubility of the double alkali thorium carbonates is the basis of an important method of separating thorium from the rare earth group. Crystalline double thorium carbonates, such as $3\,Na_2CO_3 \cdot Th(CO_3)_2 \cdot 12\,H_2O$, may be obtained by adding alcohol to the aqueous solution of the double carbonate. Hydrates of the normal orthocarbonate, such as $ThCO_4 \cdot 2\,H_2O$, are obtained by passing carbon dioxide into thorium hydroxide under pressure. The basic carbonate, $2\,Th(OH)_4 \cdot CO_2$, is formed at atmospheric pressure.

Thorium oxalate, $Th(C_2O_4)_2 \cdot 6\,H_2O$, is precipitated as a white amorphous powder when oxalic acid is added to a solution of a thorium salt. It dissolves readily in solutions of ammonium carbonate and ammonium oxalate, but is less soluble in sulfuric acid than the rare earth oxalates and is insoluble in nitric acid. Double alkali oxalates, acid oxalates, and mixed salts have been prepared.

Sulfur forms ThS$_2$, which is best prepared by the action of hydrogen sulfide on a hot mixture of ThCl$_4$ and NaCl. It forms large brown crystals, which react violently with nitric acid. ThOS is formed at the same time as small orange-yellow crystals. The two products may be separated by a sieve.

The sulfate, Th(SO$_4$)$_2$, may be prepared by heating the hydrated salts at 400°. The anhydrous salt is a white crystalline powder which is extremely soluble in ice water and forms highly supersaturated solutions. From these hydrates with 2, 4, 6, 8, or 9 molecules of water separate at various temperatures. The solutions of thorium sulfate are considerably hydrolyzed, the $\frac{N}{64}$ solution being 46 per cent hydrolyzed.

There are also formed the acid salt, $Th(SO_4)_2 \cdot H_2SO_4$, and a basic salt, $ThO_2 \cdot SO_3$, which has several hydrates; double alkali sulfates of the formula $Th(SO_4)_2 \cdot 2\,M_2'SO_4 \cdot 2\,H_2O$, of which the potassium, rubidium, and caesium salts are difficultly soluble and formed by precipitation; double salts with the sulfates of organic bases, such as pyridine, quinoline, diethylamine, and phenylhydrazine.

The sulfite, $Th(SO_3)_2 \cdot H_2O$, is prepared by warming a mixture of thorium sulfate and sulfurous acid. It is soluble in solutions of the alkali sulfites from which basic double sulfites separate on standing.

No thiosulfate has been prepared.

Thorium forms a silicide, $ThSi_2$,[1] two borides,[2] ThB_4 and ThB_6, a selenate, $Th(SeO_4)_2 \cdot 9\,H_2O$, and a selenite, $Th(SeO_3)_2 \cdot H_2O$, besides numerous salts of organic acids.

Detection. — From solutions of thorium salts, $Th(OH)_4$ is precipitated by alkali hydroxides, ammonia, or ammonium sulfide and the precipitate does not dissolve in an excess of the precipitant. Sodium thiosulfate precipitates a mixture of the hydroxide and sulfur, while sodium azide, NaN_3, precipitates the hydroxide from boiling solution. The latter test is distinctive if the ceric salts are first reduced to the cerous condition. H_2O_2 precipitates the peroxide from a warm slightly acid solution. A solution of potassium iodate containing considerable concentrated nitric acid precipitates thorium iodate, insoluble in oxalic acid; cerium must be in the trivalent condition; zirconium iodate precipitates but dissolves in oxalic acid. Sodium hypophosphate precipitates on boiling the hypophosphate of thorium from very dilute thorium solutions, even in the presence of concentrated hydrochloric acid; ceric, zirconium, and titanium salts must be absent. Sodium pyrophosphate precipitates the thorium salt, sparingly soluble in dilute mineral acids; zirconium and ceric salts must be absent. Oxalic acid precipitates thorium, insoluble in excess of reagent, while zirconium oxalate is soluble in excess. Ammonium oxalate precipitates the oxalate soluble in excess, and not reprecipitated on dilution, while rare earth oxalates reappear on dilution. HCl reprecipitates thorium oxalate from solutions of its double oxalate, while zirconium does not.

Estimation. — The quantitative determination of thorium in a solution free from zirconium and the rare earth group is very simple. It consists of precipitating the hydroxide or oxalate and igniting to the oxide. In the presence of other similar salts the process becomes elaborate and usually involves several precipitations by the same or different reagents in order completely to remove interfering substances. Some of the more important methods of determination are outlined as follows: —

(1) Hydrogen peroxide added to a neutral solution of the nitrates containing NH_4Cl or NH_4NO_3 precipitates thorium completely.[3] The precipitate may be ignited directly or dissolved in HCl and reprecipitated by ammonia.

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[1] Hönigschmidt, *Compt. rend.* **142** 157 (1906).

[2] *Ibid.* **141** 191 (1905).

[3] *Zeit. angew. Chem.* **15** 297 (1902) and *Compt. rend.* **127** 412 (1898).

(2) The iodate method[1] is available in the presence of phosphoric acid, so may be applied directly to a solution of monazite in sulfuric acid. Add HNO_3 to the sulfuric acid solution, then KIO_3 and HNO_3. Repeat the precipitation and finally dissolve the thorium iodate in HCl, precipitate as $Th(OH)_4$, and ignite.

(3) If a little H_2O_2 is added to an acid solution containing thorium, then the solution brought to a boil and a solution of sodium hypophosphate[2] added drop by drop as long as a precipitate forms, thorium hypophosphate is precipitated along with zirconium. Treat the precipitate with a mixture of sulfuric and nitric acids, evaporate to dryness, take up with water and precipitate thorium oxalate; ignite and weigh as ThO_2.

A volumetric method is based on the fact that ammonium molybdate precipitates thorium as the normal molybdate but has no action on the rare earth elements.[3] The mixed nitrates are dissolved in 1 : 15 acetic acid to which a little sodium acetate has been added. This solution is titrated cold with ammonium molybdate, using diphenylcarbazide as an outside indicator. The end point is the appearance of a deep rose color which fades quickly. Another volumetric method[4] precipitates thorium from a mixed nitrate solution with hot oxalic acid; let stand, filter, wash, and add the precipitate to hot water, then add 1 : 1 sulfuric acid and titrate with decinormal permanganate.

Thorium may also be determined quantitatively by measuring the radioactivity of the ore or compounds.[5]

The use of cupferron for the determination of thorium is not successful.[6]

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[1] *Chem. Zeit.* **34** 306 (1910).

[2] *Chem. Zeit.* **36** 686, 821 (1912); *Zeit. angew. Chem.* **25** 1678 (1912).

[3] Metzger and Zons, *Jour. Ind. and Eng. Chem.* **4** 493 (1912).

[4] Gooch and Kobayoshi, *Am. Jour. Sci.* **45** 227 (1918).

[5] *Jour. Am. Chem. Soc.* **41** 42 (1919); **43** 2003 (1921); Borgström, *Finska Kem. Meddel* 1917; C. A. **15** 1677 (1921).

[6] *Jour. Ind. and Eng. Chem.* **12** 344 (1920).

CHAPTER XI

GROUP IV — GERMANIUM

THE elements carbon, silicon, germanium, tin, and lead comprise Division B of Group IV. As a group these elements resemble the members of the A division in general, there being fewer contrasts between the two divisions than in any other family of the periodic table. Elements of Division B are somewhat less electropositive than the corresponding members of Division A. Division B elements form no superoxides but do form organo-metallic derivatives.

There is a close family relationship between the members of Division B, whose physical properties, so far as they are known, show a gradual change with increasing atomic weight. (See Table XXIX.) The chemical properties likewise show interesting family relationships. All the elements of the family form both bivalent and tetravalent compounds and in all cases

TABLE XXIX

Properties of the Carbon-Lead Family

	CARBON	SILICON	GERMANIUM	TIN	LEAD
Atomic Weight	12.005	28.1	72.5[1]	118.7	207.2
Specific Gravity	2.3–3.5	2.35	5.47	5.8–7.3	11.4
Atomic Volume	4.5	12.04	13.26	18.25	18.18
Melting Point		About 1500°	953°–963°	231°	326°
Boiling Point		About 3000°		220°	1500°
Boiling Point MCL_4	76°	59°.6	86°	113°.9	Decomposes

[1] Müller, *Jour. Am. Chem. Soc.* **43** 1085 (1921) finds 72.42.

except lead the compounds of the higher valence are more important and more characteristic. Carbon and silicon are acid-forming while germanium, tin, and lead are increasingly basic in character, as is shown by a comparison of the halides, the monoxides, and the dioxides. The tetrachlorides are increasingly hydrolyzed by water as the atomic weight of the element increases, but the dichlorides of the heavier elements are the most stable. Tin and lead are known in similar allotropic forms. Lead resembles thallium and bismuth, forming a link between this family and its neighbors of the periodic system. Like many of the other elements of high atomic weight it has peculiarities which differentiate it from the other members of its family. Its relationship to radioactive elements is pretty definitely established.

Historical. — The element ekasilicon was predicted by Mendeleeff and its general physical and chemical properties foretold. (See Table III, p. 8.) No element was discovered which fulfilled these prophecies until 1886, when Clemens Winkler was analyzing the newly discovered silver mineral argyrodite. The total constituents added up gave between 93 and 94 per cent. He repeated the analysis carefully several times and obtained good checks but could not find any known element which made up the balance of the mineral. After much careful work he discovered that when the mineral was heated out of contact with the air, there was formed a dark brown sublimate, which he proved was made up of the sulfides of mercury and a new element for which he proposed the name germanium. On further study he found that it presented close agreement with Mendeleeff's ekasilicon.[1] The mineral upon which he was working appears to have been a mixture of argyrodite and other minerals[2] so that it probably contained not more than 0.02–0.03 per cent of germanium. From this material he extracted 180 grams of the pure element.

Germanium is one of the least known of all the elements, since almost all of our knowledge concerning it has been furnished by the researches of its discoverer.[3]

Occurrence. — Germanium is a very rare element, found in only a few minerals. It is usually found in nature as the sulfide and is very commonly associated with silver sulfide. The principal ore is argyrodite, containing 6.93 per cent germanium. This ore comes from a Freiberg, Saxony, mine and is very similar to canfieldite, 6.55 per cent germanium, found in

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[1] See Roscoe and Schorlemmer, Vol. 2, p. 70.

[2] Urbain, *Compt. rend.* **150** 1758 (1910).

[3] *Jour. Ind. and Eng. Chem.* **9** 601 (1917).

Bolivia. A recently discovered[1] mineral, ultra-basite, from Freiberg, is thought to be a mixture of the sulfides of germanium, silver, lead, and antimony, containing 2.2 per cent germanium. This element is also found in smaller amounts in zinc blende from various sources. Urbain examined[2] 64 samples of blendes from as many localities and reports some germanium in 38 of them. From 550 kilograms of a Mexican blende he obtained 5 grams of pure germanium.[3] It is also found in some samples of tantalite, columbite, cassiterite[4] and such rare earth minerals as euxenite, samarskite,[5] gadolinite, and fergusonite. Traces have also been detected in certain mineral waters. From 250,000 liters of a certain French mineral water, Bardet obtained[6] 60 mg. GeO_2.

The richest sources of germanium now known are the spelter residues from certain American zinc ores,[7] especially those from Wisconsin and Missouri. It collects in the spelter retort residues, since the oxide is easily reduced by carbon at red heat and the metal is only slightly volatile at 1350°. In the zinc oxide furnaces, germanium burns to GeO_2 and passes off with the dust to the bag houses. Probably the ores of Wisconsin and Missouri contain not more than 0.01 per cent germanium, but the amount seems to be more uniform in the case of this element than it does in the case of gallium.

Extraction. — Germanium ores may be decomposed in a number of ways. (1) The mixed sulfides may be dissolved in strong sulfuric acid and evaporated to dryness. If the sulfates are taken up with water and treated with sodium sulfide, both zinc and germanium are precipitated. The former may be dissolved in sulfuric acid (15 : 100) while the germanium sulfide remains in solid form.[8] (2) A more satisfactory separation is usually accomplished by suspending the oxides in 1 : 2 HCl and saturating with H_2S. Filter, wash with dilute HCl, and

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[1] *Zeit. Kryst. Mineralogie,* **55** 430 (1921).

[2] *Compt. rend.* **149** 602 (1909).

[3] Urbain, Blondel, Obiedoff, *Compt. rend.* **150** 1758 (1910).

[4] Hadding, *Zeit. anorg. allgem. Chem.* **123** 171 (1922).

[5] Dennis and Papish have shown that American samarskite does not contain a detectable quantity of germanium; *Jour. Am. Chem. Soc.* **43** 2131 (1921).

[6] *Compt. rend.* **158** 1278 (1914).

[7] See Hillebrand and Scherrer, *Jour. Ind. and Eng. Chem.* **8** 225 (1916) and also *ibid.* **9** 661 (1917).

[8] Urbain, *Compt. rend.* **150** 1758.

dissolve the precipitate in Na_2S. Bring the solution to the neutral point by adding dilute H_2SO_4 and let stand. Filter off the precipitated sulfides of tin, arsenic, and antimony; to the filtrate add an equal volume of strong HCl and saturate the solution with H_2S, when pure GeS precipitates.[1] (3) To separate germanium from ZnO, the ore may be added in small portions to commercial hydrochloric acid[2] in the proportion of a kilogram of oxide to 2400 cc. of acid. After the solid is dissolved add $KClO_3$ cautiously until the oxides of chlorine begin to appear, then distill at once. $GeCl_4$ distills under these conditions, between 120°–140°. (4) From argyrodite germanium may be extracted by fusion with sodium carbonate and potassium nitrate. Cool the melt, pulverize, and extract the alkaline germanate with water, add sulfuric acid and evaporate till all nitric acid is expelled. If the residue is dissolved in water and allowed to stand, germanium oxide separates from the solution.

Separation. — From most of the metals, germanium may be separated by the formation of the sulfo-salts with ammonium sulfide. It may be separated from arsenic, antimony, and tin by exactly neutralizing the sulfo-salts with sulfuric acid and filtering after 12 hours. Evaporate to small bulk, add ammonia, ammonium sulfate, and sulfuric acid and saturate with H_2S. GeS_2 precipitates while the other metals remain in solution.

Germanium may also be separated from arsenic by either of three methods: (1) Fuse the mineral[3] with Na_2CO_3 and S, forming the sulfo-salts, add $NH_4C_2H_3O_2$, acidify with $HC_2H_3O_2$, and saturate with H_2S. Under these conditions arsenic is completely precipitated and germanium remains in solution. (2) Germanium chloride may be distilled in the presence of strong HCl by oxidizing arsenic to the less volatile pentachloride by means of a chromate.[4] In this manner 0.5 mg. of GeO_2 mixed with 100 mg. As_2O_3 gave an arsenic-free germanium chloride. The completeness of the separation by distillation has been questioned.[5] (3) If the oxides are dissolved in an excess of

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[1] Truchot, *Les Terres Rares*, p. 294.

[2] James, *Jour. Am. Chem. Soc.* **41** 947 (1919).

[3] Browning, *Am. Jour. Sci.* **44** 313.

[4] Browning, *ibid.* **45** 663.

[5] J. H. Müller, *Jour. Am. Chem. Soc.* **43** 1085 and 2549 (1921); see also Dennis and Papish, *ibid.* **43** 2131 (1921).

HF and H_2S is added, As_2S_3 is quantitatively precipitated while germanium is left in solution.[1]

From lead, cadmium, and selenium, germanium may be separated[2] by distilling a strong hydrochloric acid solution in the presence of a little $KMnO_4$, MnO_2, or $KClO_3$. The delivery tube should end just above the surface of the water in the receiver, which is surrounded by a cooling mixture. A precipitate of GeS_2 may be obtained by saturating with hydrogen sulfide.

Metallurgy. — The metal may be prepared by: (1) heating the oxide with carbon; (2) reducing potassium fluogermanate, K_2GeF_6, with hydrogen or sodium; (3) heating the oxide in a stream of hydrogen; or (4) reducing the oxide with magnesium.

Properties. — Germanium is a grayish white metal with a brilliant metallic luster, crystallizing in regular octahedra.[3] The specific resistance at 0° is 0.089 ohms per cubic centimeter.[4] Thermoelectric determinations indicate that germanium exists in more than one form. It is brittle, has a density of 5.469 at 20°, and melts at about 958°.[5] Its boiling point has not been determined definitely. In the presence of the oxide it begins to vaporize at a temperature as low as 750°, but in an atmosphere of hydrogen or nitrogen it produces little vapor at 1350°. The specific heat 0°–100° is 5.34. It is stable in the air at ordinary temperatures but when heated it burns to GeO_2. It is not acted upon by hydrochloric acid, but dissolves readily in aqua regia; toward nitric acid it behaves much like tin, being oxidized to GeO_2. It is dissolved by sulfuric acid, which it partially reduces, liberating sulfur dioxide. It combines directly with the halogens.

Uses. — Recently some success has been met in the treatment of anemia by means of germanium compounds.[6]

Compounds. — Germanium forms two series of compounds. In the germanous compounds the element has a valence of 2. These compounds are not numerous, are quite unstable, and resemble the compounds of silicon and carbon. In the ger-

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[1] J. H. Müller, *ibid.* **43** 2549 (1921).

[2] Browning, *Am. Jour. Sci.* **44** 331.

[3] See Albert W. Hull paper read before the American Physical Society at Washington; note *Chem. and Met. Eng.* **26** 1024 (1922).

[4] Bidwell, *Phys. Rev.* **19** 447 (1922).

[5] Biltz, *Zeit. anorg. Chem.* **72** 313 (1911).

[6] *Catalyst,* **8** No. 1, 7 (Jan. 1923); *ibid.* No. 4, 14 (Apr. 1923).

manic compounds the valence is 4, the stability greater, and the behavior more suggestive of tin and titanium.

Hydrogen forms a gaseous hydride, GeH_4, when germanium chloride is reduced by sodium amalgam or when a germanium solution is introduced into a Marsh generator. The mixture of hydrogen and GeH_4 burns with a reddish blue flame which deposits a mirror on a cold surface. This is soluble in sodium hypochlorite solution. When the gas is heated in a tube it decomposes, forming a deposit which is red by transmitted light and green by reflected light. When GeH_4 is bubbled through a silver nitrate solution, silver germanide is precipitated. Concentrated nitric acid converts this into GeO_2.

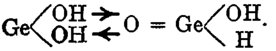
Germanium chloroform, $GeHCl_3$, is formed when hydrogen chloride is passed over slightly heated germanium powder. It is a vapor which forms a volatile, colorless liquid, by cooling with ice. On exposure to air it becomes turbid, due to formation of $GeOCl_2$, and it reacts with water, forming $Ge(OH)_2$.

Germanium tetraethyl, $Ge(C_2H_5)_4$, was foretold by Mendeleeff and shows the ability of germanium to form volatile organo-metallic compounds. It is formed by the reaction of germanic chloride and zinc ethyl in an atmosphere of carbon dioxide. It is a colorless liquid with a boiling point of 160°. It is lighter than water with which it does not mix. The vapor burns readily, forming an explosive mixture with oxygen.

Oxygen forms two compounds with germanium.

Germanous oxide, GeO, is a dark gray powder which is obtained by heating $Ge(OH)_2$ in an inert atmosphere or by reducing GeO_2 with germanium or magnesium. It is volatile and dissolves in hydrochloric acid.

Germanous hydroxide, $Ge(OH)_2$, is precipitated when an alkali is added to a solution of germanous chloride. It is soluble in excess of alkali. When first precipitated it is distinctly yellow in color, but on heating it turns red. This change is believed to indicate a tautomeric change,



$\mathrm{Ge}\begin{matrix}\diagup \mathrm{OH} \rightarrow \\ \diagdown \mathrm{OH} \leftarrow \end{matrix}\mathrm{O} = \mathrm{Ge}\begin{matrix}\diagup \mathrm{OH} \\ \diagdown \mathrm{H} \end{matrix}.$

The latter is a germanium analogue of formic acid. This view is strengthened by the fact that germanium chloroform is hydrolyzed, giving germanous hydroxide: $HGeCl_3 + 2\,HOH = HGeOOH + 3\,HCl$. It has been shown[1] that certain metallic hydroxides behave as feeble acids and that the order of increasing strength as acids is zinc, beryllium, lead, stannous and germanous hydroxides. In the acidic compounds of the last three, the elements become quadrivalent. By studying the electrical conductivities and the rate of hydrolysis of ethyl acetate, it appears that germanous hydroxide is slightly weaker as an acid than acetic acid.

Germanic oxide, GeO_2, is prepared by direct union of the elements, by igniting the sulfide or oxidizing it with nitric or sulfuric acid, or by adding acids to dilute alkaline solutions of germanium salts. It is a dense white powder, which melts to a clear liquid, but is not volatile at 1025°. It is sparingly soluble in water, forming an acid solution, from which it crystal-

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[1] Hantzsch, *Zeit. anorg. Chem.* **30** 289 (1902).

lizes in small rhombic crystals. It dissolves with some difficulty in acids, forming germanic salts, and in alkalies, forming germanates. Neither $Ge(OH)_4$ nor $GeO(OH)_2$ is known.

Fluorine forms both GeF_2 and GeF_4, the former by reduction of K_2GeF_6 with hydrogen and the latter as the trihydrate, when a solution of GeO_2 in HF is evaporated over sulfuric acid. $GeF_4 \cdot 3\ H_2O$ forms hygroscopic crystals, easily soluble in water, but it is somewhat hydrolyzed.

Fluogermanic acid, H_2GeF_6, is formed by passing the vapor of GeF_4 into water. If KOH is added to the solution, potassium fluogermanate, K_2GeF_6, is formed. When KCl and HF are added to a solution of $GeCl_4$, a characteristic gelatinous precipitate of K_2GeF_6 is produced. On standing the precipitate becomes crystalline, isomorphous with ammonium fluosilicate.

Chlorine forms $GeCl_2$, $GeCl_4$, and $GeOCl_2$.

Germanous chloride is made by passing hydrogen chloride over heated GeS. It is a colorless liquid, which fumes in moist air and is completely hydrolyzed by water. It is soluble in concentrated hydrochloric acid, its solution acting as a powerful reducing agent.

Germanic chloride, $GeCl_4$, is prepared by burning the metal in chlorine,[1] or by heating the metal or its disulfide with mercuric chloride. It is a thin colorless liquid which fumes in moist air and emits a crackling sound when mixed with water. It melts at −49.5° and has a specific gravity of 1.874. It does not react with H_2SO_4; it is slowly decomposed by nitric acid and reacts vigorously with ammonia and the alkalies.

Germanium oxychloride, $GeOCl_2$, is prepared by oxidation of germanium chloroform by warming the latter or bubbling air through it. It is a colorless oily liquid which does not fume in the air.

Bromine and iodine unite directly with germanium, forming $GeBr_4$,[2] and GeI_4,[3] which resemble the corresponding chloride.

Sulfur forms GeS and GeS_2.

Germanous sulfide, GeS, is prepared by heating GeS_2 with the metallic germanium in an inert atmosphere, or by partially reducing GeS_2 in hydrogen. GeS may be precipitated by adding H_2S to a germanous solution. The precipitated form is a dark red amorphous powder, and that prepared in the dry way forms metallic-looking crystals, dark gray in color by reflected light and red by transmitted light. It may be melted and vaporized without decomposition, so it is the most definite germanous compound. It is slightly soluble in water, and dissolves in acids, alkalies, and yellow ammonium sulfide, forming with the latter a characteristic sulfo-salt of GeS_2.

Germanic sulfide, GeS_2, occurs in nature and is prepared by adding H_2S to a solution of a germanic salt or by acidifying a solution of GeS in ammonium sulfide. For the latter an excess of strong mineral acid is necessary because the sulfo-acid is quite stable. GeS_2 is a white powder

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[1] Dennis and Hance, *Jour. Am. Chem. Soc.* **44** 299 (1922).

[2] Dennis and Hance, *loc. cit.*

[3] Dennis and Hance, *Jour. Am. Chem. Soc.* **44** 2854 (1922).

which does not mix readily with water. It dissolves slightly in water, but the solution evolves H_2S because of the hydrolysis which takes place.

Detection. — Germanium compounds give characteristic blue and violet lines in the spark spectrum; the blue line λ 4686 is especially characteristic.[1]

Germanous solutions are identified by the precipitation (1) of the yellow hydroxide with alkalies, (2) of brown GeS with H_2S, (3) of the white ferrocyanide with $K_4Fe(CN)_6$. They also reduce chromate and permanganate solutions and precipitate metallic gold from the chloride.

Germanic solutions are characterized by the formation with H_2S of a white sulfide, GeS_2, soluble in ammonium sulfide, also by the formation of a gelatinous precipitate, K_2GeF_6, when KCl and HF are added to GeF_4. This precipitate becomes crystalline on standing. The hydrated dioxide is partially precipitated by ammonia, ammonium carbonate, and sodium carbonate. The fixed alkalies produce no precipitate because of the ready formation of the germanates.

Estimation. — For the quantitative determination of germanium the element is usually precipitated as GeS_2 and weighed as such or converted to GeO_2 by nitric acid and then weighed.[2] Magnesia mixture precipitates Mg_2GeO_4, which may be filtered, ignited, and weighed as the orthogermanate.[3]

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[1] Jacob Papish, *Chem. News*, **124** 3 (1922).

[2] Dennis and Papish, *Jour. Am. Chem. Soc.* **43** 2131 (1921).

[3] Müller, *Jour. Am. Chem. Soc.* **44** 2493 (1922).

CHAPTER XII

GROUP V — VANADIUM

THE elements of Group V are easily divided into two families, vanadium, columbium, and tantalum making up Division A, and phosphorus, arsenic, antimony, and bismuth comprising Division B. Nitrogen is an introductory element which resembles both divisions in some ways, but differs from each in other characteristics. These two sub-groups resemble each other in many respects, especially in their chemical properties. All the elements of the group form an oxide, M_2O_5, which is strongly acidic in the case of elements of low atomic weight but with decreasing acidity as atomic weight increases, until Bi_2O_5 can scarcely be called acidic at all. All the elements of the group form two definite series of compounds, one trivalent and the other pentavalent. Valences of 2 and 4 are also common. This group is especially characterized by the large number of oxides and halides which its members form.

Members of the two divisions have much greater differences than are shown by the two divisions of Group IV. Thus if we consider nitrogen as an introductory element, we find that phosphorus, arsenic, antimony, and bismuth are easily reduced from their oxides, melt at relatively low temperatures, and vaporize easily. Phosphorus has the characteristics of a non-metal, but metallic properties increase with increasing atomic weight, bismuth presenting fairly typical metallic properties. All the members of this division form organo-metallic derivatives and all except bismuth form very characteristic volatile hydrogen compounds. All the members of Division B are well-known chemical elements which have found numerous applications in the industries.

In contrast to these characteristics the three members of Division A are extremely difficult to reduce from their oxides and have high melting and boiling points. They are all typically metallic in appearance and general behavior. Vanadium is less basic than columbium and tantalum, as is to be expected, but there is not a regular increase of basicity with increased atomic weight. Considering that columbium forms oxy-salts more readily than does tantalum and that tantalum halides are completely hydrolyzed while the columbium compounds are hydrolyzed only to the oxy-salts, it appears that tantalum in some respects is somewhat less metallic than columbium. These three elements do not form volatile compounds with hydrogen. All members of Division B may be considered rare, at least in the sense that they have only recently come to attract the attention of chemists.

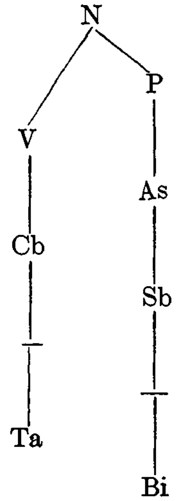

Fig. 12

The relationship between the members of the two divisions is shown in Fig. 12. The blank spaces following columbium and antimony may possibly represent elements not yet discovered, but the proximity of the rare earth group makes it seem probable that these spaces do not represent missing chemical individuals. The close resemblance between columbium and tantalum is hardly suggestive of a missing intermediate element, while there is greater reason for expecting an element to fall between antimony and bismuth.

The physical properties of the members of Division A are shown in Table XXX.

Table XXX

Physical Properties of the Vanadium Family

	Vanadium	Columbium	Tantalum[1]
Atomic Weight	51.0	93.1	181.5
Color.	Silvery	Steel-gray	Iron-gray
Specific Gravity	5.5	7.06	8.0
Atomic Volume	9.3	13.3	23.0
Melting Point	1720°	1950°	About 2910°

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[1] For additional properties of tantalum see table by C. W. Balke, *Chem. and Met. Eng.* **27** 1273 (1922).

VANADIUM

Historical. — In 1801 Del Rio announced the discovery of a new metal which he had found in a certain lead ore from Zimapan, Mexico. He suggested the name erythronium, meaning red, because its salts became red when heated with acids. In 1805 Collet-Descotils concluded that this new metal was an impure oxide of chromium and Del Rio accepted this conclusion. But in 1830 Sefström found a new metal in a Swedish iron ore, which he proposed to call vanadium after the name Vanadis, the Scandinavian goddess more frequently known as Freya. During the same year Wöhler showed that Del Rio's erythronium was a new element identical with vanadium and that the Mexican ore was a lead salt of this element. Berzelius took over Sefström's material, and in 1831 published the results of his extensive investigation. He concluded that vanadium belonged in the group with chromium and molybdenum because of its acidic trioxide. This view was accepted till 1867, when Roscoe showed that the element belongs with phosphorus and arsenic, that the volatile chloride contains oxygen and is analogous to $POCl_3$, and that Berzelius' metal was either the oxide VO or the nitride, depending on the method of preparation.

Occurrence.[1] — Although commercial vanadium ores are found in only a few localities, the element is estimated to comprise 0.017 per cent of the earth's crust and is known in a large number of rare minerals. It is generally present as a vanadate, though in some important minerals it is found as silicate, sulfide, or oxide. The more important minerals are: —

Vanadinite, $3\,Pb_3(VO_4)_2 \cdot PbCl_2$ or $(PbCl)Pb_4(VO_4)_3$, is the mineral from which Del Rio first obtained vanadium material. It contains from 8 to 21 per cent V_2O_5, varies in color from deep ruby red to a straw yellow, and is found in Mexico, Urals, Sweden, Argentina, and abundantly in the mining regions of Arizona and New Mexico.

Descloizite, $4\,(PbZn)O \cdot V_2O_5 \cdot H_2O$, contains 20–22 per cent V_2O_5, cherry red to reddish brown, found in New Mexico and Arizona.

Carnotite is a potassium uranyl vanadate for which the formula $K_2O \cdot 2\,UO_3 \cdot V_2O_5 \cdot 8\,H_2O$ is frequently given. The ore, however, varies materially from this composition. It contains 19 or 20 per cent V_2O_5 and is valuable for both vanadium and uranium, as well as radium. It occurs extensively in Paradox Valley, Colorado, and in Utah, South Australia, Portugal, etc.

Roscoelite is a silicate of doubtful formula, probably a mus-

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[1] W. F. Hillebrand, *Jour. Am. Chem. Soc.* **29** 1019 (1907) and *Eng. and Min. Jour.* **93** 1093 (1912).

covite mica in which a part of the aluminium is replaced by vanadium. It is found in San Miguel County, Colorado, and is the most important simple vanadium ore in the United States.

Patronite is a sulfide of vanadium as associated with pyrite and a carbonaceous substance which contains much free sulfur. It varies widely in composition, but a typical analysis gives vanadium sulfide 35 per cent, iron pyrite 5 per cent, free sulfur 35 per cent, and silica 15 per cent, with small amounts of molybdenum, nickel, aluminium, calcium, etc. It is found in the Andes Mountains, especially in Peru.

Asphaltite is an extremely soft, friable deposit of low specific gravity, containing 80 per cent hydrocarbons, but yielding an ash which contains from 5 to 50 per cent V_2O_5. It is found near Page, Oklahoma, and Palisade, Nevada, but the main deposit is in Peru.

In addition to these commercial ores, vanadium is found occasionally as vanadic ocher, V_2O_5, bismuth ocher containing 1–29 per cent V_2O_5, and many others, still more rare. It is almost always present in rutile, which may owe its color to the vanadium rather than to the iron content. Traces have been found in certain copper and iron ores, in many clays, especially fire clays, in trap and basalt, and in certain coal deposits. The ash from an Oklahoma coal shows varying amounts of vanadium, sometimes running as high as 34.5 per cent V_2O_5. Ash from some Peru and Argentine coals may contain as much as 38 per cent V_2O_5. Vanadium has recently been found in the blood of certain fish, where it evidently replaces iron. A brown spotted holothurian, Sticopus möbii, from the Tortugas, showed 0.0247 g. of vanadium in 20 g. of the dried animal body.[1] Two other species of holothurians showed no vanadium, but this element has been detected in the blood cells of certain ascidia taken from the Bay of Naples.

The world's most important vanadium supply comes from Peru, which formerly supplied 70 per cent of the world's vanadium.[2] The raw ore averages 20–25 per cent V_2O_5, but before shipment this is increased to 35–40 per cent by calcination. Occasionally small quantities will run as high as 50 per cent. The mines are high in the mountains, being about 15,000 feet above sea level. Transportation was formerly by llamas and boat, but recently a system of motor trucks and a narrow-gauge railroad has been provided. The annual shipments have shown considerable fluctuation due to exhaustion of some of the rich-

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[1] *Am. Jour. Sci.* **46** 473.

[2] See Hewett, *Trans. Am. Inst. Min. Eng.* **40** 291 (1909); Hillebrand, *Jour. Am. Chem. Soc.* **29** 1019 (1907); Wilson, *Chem. and Met. Eng.* **26** 699 (1922).

est deposits of patronite, as well as difficulties of transportation. Peru in 1919 supplied 60 per cent of the world's vanadium, nearly all of which was shipped to the United States. The largest domestic deposits are in San Miguel County, southwestern Colorado, about 36 per cent of the world's vanadium coming from Vanadium, Colorado. These deposits are mainly roscoelite with a little carnotite, averaging 1.5 per cent V_2O_5, but the deposits are large and easily worked.[1] At Cutter, New Mexico, there are vein deposits of vanadinite, but the ore is a difficult one to work. Small amounts of vanadium are obtained from the slags of certain iron ores, especially Swedish magnetite.[2]

Previous to 1906 Spain was the greatest producer of vanadium. The deposits are vanadinite in sandstone, containing an average of 3 per cent V_2O_5, which is raised to 14 per cent by concentration. Other deposits are found in Mexico, Argentine, England, Sweden, Russia, and Germany.

Extraction.[3] — The method used in extracting vanadium from its ores varies widely with the nature and richness of the ore and the value of the by-products. The difficulties encountered are mainly in connection with the purification of vanadium from uranium, aluminium, iron, and silica. It is probable that no two mills use exactly the same process. In general the methods [4] use (1) an acid method, producing soluble vanadyl compounds; or (2) an alkali method, producing soluble alkali vanadates. The following outline methods illustrate the general principles employed: —

(1) The Koenig process consists in treating the crushed ore with a 20 per cent solution of sulfuric or hydrochloric acid at a temperature of 200° and a pressure of 225 pounds per square inch. After several hours the liquid is filtered, evaporated, and the salts ignited to expel excess acid, then roasted with sodium carbonate. The mass is leached with boiling water, and carbon dioxide bubbled in to precipitate alumina. This method is recommended for roscoelite and vanadium-bearing sandstone.

(2) The Fleck process, which may be used upon carnotite

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[1] See U. S. Bur. of Mines, *Bull.* 70, p. 51.

[2] Kjellberg, *Jernkontorets Annalen* (1921), p. 147.

[3] See *Bull.* 104, U. S. Bur. of Mines; Bleecker, *Chem. and Met. Eng.* **11** 501 (1911).

[4] See *Bull.* 104, U. S. Bur. of Mines.

ores, consists in treating the finely ground ore with dilute sulfuric acid. The iron and vanadium present in the solution are reduced by sulfur dioxide, then sufficient powdered limestone added to precipitate the calcium. Next the uranium and vanadium are precipitated by boiling the solution with more limestone.

(3) The U. S. Bureau of Mines nitric acid method of treating carnotite is outlined in the diagram, Fig. 13. This method is said to extract as much as 90 per cent of the radium and nearly all of the uranium, but some vanadium is left in the residues, especially if roscoelite and similar vanadium ores are present in the carnotite. This method is especially recommended on account of the high recovery of radium. Its cost is greatly reduced by the fact that enough nitric acid is recovered to disintegrate the ore, but in spite of this saving it is relatively expensive.

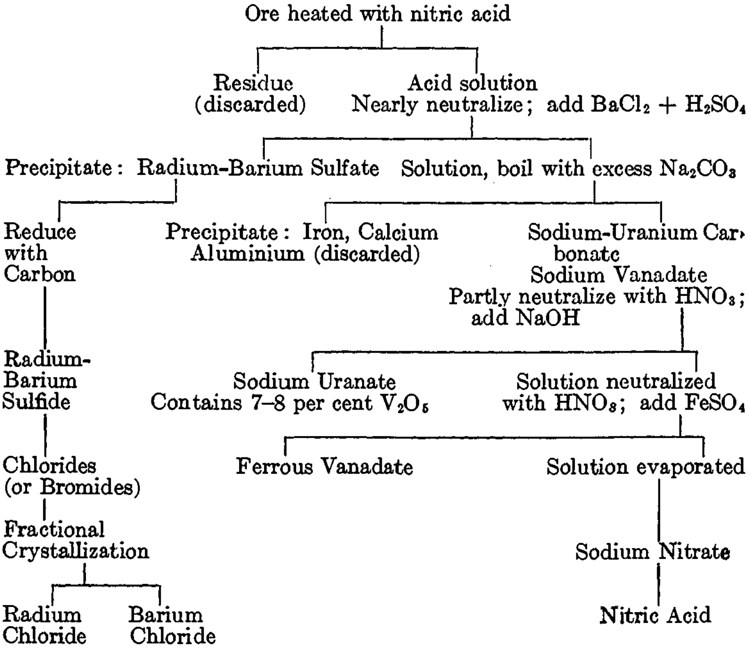

FIG. 13

(4) For vanadinite ores experimental work done at the

Bureau of Mines[1] shows that an efficient method of extracting the valuable constituents is as follows: flux the ore with soda ash, when the lead is recovered as a metal; from the slag vanadium and molybdenum are extracted with water and calcium vanadate precipitated with slacked lime, while the molybdenum remains in solution. Vanadinite ores may also be ground and extracted with sodium sulfide, when lead sulfide precipitates and sodium vanadate dissolves, free from sulfides. By adding NH_4Cl a precipitate of $(NH_4)_3VO_4$ is formed, or after purification $Fe_3(VO_4)_2$ is precipitated by adding $FeSO_4$, or V_2O_5 is precipitated by acidification.

(5) From the cupro-descloizite of Brisbee, Arizona, vanadium may be extracted by the sulfuric acid leach, but a better method is a combination of nitrate fusion and sulfuric acid leach,[2] in which the cost of treatment is less than the by-products recovered.

The method formerly used by the Primos Chemical Company at Newmire, Colorado, depends on fusing the crushed roscoelite with sodium chloride. The sodium vanadate formed is dissolved out and ferrous sulfate added to precipitate ferrous vanadate. The uranium is not recovered by this process. Other similar processes fuse the ore with an alkali carbonate and carbon,[3] sodium nitrate, or potassium acid sulfate.

(6) The Haynes-Engle process consists in digesting the coarsely ground ore with a solution of sodium carbonate until the uranium and vanadium are extracted. Sodium hydroxide is added to precipitate sodium uranate and slaked lime to precipitate the vanadium.

Vanadium is obtained from many of the extracts, either by precipitation as ferrous vanadate or calcium vanadate or by electrolytic deposition. If ferrous sulfate is used, it must be present in considerable excess in order to prevent loss of vanadium. The electrolytic deposition has some advantages over the precipitation methods, but it does not produce a pure product. If ferrous vanadate is desired, a nearly neutral solution is used, the anode is iron and the cathode almost any metal. A potential difference between the electrodes of four volts is suffi-

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[1] J. E. Conley, *Chem. and Met. Eng.* **20** 514 (1919).

[2] *Ibid.* **20** 465 (1919).

[3] Herrenschmidt *Compt. rend.* **139** 635 (1904).

cient to cause the vanadium to collect around the anode. For the precipitation of vanadic acid a strong mineral acid may be added to a solution of sodium vanadate, but about 10 per cent of the vanadium cannot be removed in this manner. Vanadic acid may be obtained by heating ammonium metavanadate or adding hot HCl to dry calcium vanadate. In one electrolytic method, vanadic acid is precipitated in a porous cell which is surrounded by water that has been made slightly alkaline. The solution is hot and contains a slight excess of sodium carbonate. A platinum anode, an iron cathode, and a potential difference of 6 to 8 volts are used. This method yields a product which is 98 per cent pure.

Metallurgy. — Metallic vanadium may be prepared in a number of ways. (1) By reduction of vanadium dichloride by pure hydrogen. This method is difficult to use because at red heat vanadium unites readily with oxygen and water, so both must be carefully excluded. (2) By making a plastic mass of vanadium pentoxide with carbon and paraffin, shaping into rods and passing the electric current through them in a vacuum. (3) By reduction of the pentoxide with misch metal [1] or silicon. (4) By reduction of the trioxide with carbon.[2] (5) By the thermite reduction process.[3] A product which was 99 per cent pure has been obtained by this method or by reduction with vanadium carbide. (6) By electrolysis of a solution of the trioxide in fused calcium vanadate.[4] The anode is made of carbon and the cathode is prepared by pulverizing ferrovanadium and pressing the powder into a cône-shaped form. The current density used is 4.5 amperes per square inch of anode surface.

There is relatively little interest in the production of pure vanadium, at least 90 per cent of the vanadium extracted being produced and used in the form of ferrovanadium alloys. These usually contain from 25 to 50 per cent vanadium and may be prepared by either of three methods: (1) reduction by the thermite process; (2) reduction with carbon in an electric furnace; and (3) several electrolytic methods.

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[1] Muthmann and Weiss, *Liebig Ann.* **337** 370; **355** 58.

[2] Ruff and Martin, *Zeit. angew. Chem.* **25** 49.

[3] *Zeit. anorg. Chem.* **64** 217 and 225 (1909).

[4] Gin, *Electrochem. and Met. Ind.* **1** 264 (1909).

The electrolytic methods do not seem to have been very generally used, although the product obtained is free from both carbon and aluminium. Of these methods the following illustrate the principles used: —

(1) Gin's electrolytic method for ferrovanadium[1] uses vanadic acid dissolved in a bath of fused iron fluoride and calcium carbide. The anode is a mixture of vanadic acid and retort carbon, and the cathode is fused steel. (2) A French process uses vanadic acid dissolved in calcium fluovanadate, and a current of 0.7 ampere per square centimeter of anode surface. (3) An American process electrolyzes a solution of vanadic acid in molten ferrosilicon. (4) Another American process passes an electric current through a charge made up of vanadium oxide and the calculated amounts of iron and carbon.

The reduction by means of aluminium has been the main method of producing ferrovanadium and is especially serviceable for the production of a product free from carbon. The reduction is carried out successfully in furnaces capable of producing 125,000 pounds of alloy per run.[2] The large units used give a greater uniformity to the product and a much higher temperature (2500°–2800° C.) than in small crucibles. In this way a fluid slag is produced and the separation of the metal is more complete. Not all of the vanadium is extracted by the thermit method, some being left in the slag. This process is somewhat expensive, due not only to the cost of the aluminium but more especially because of loss of this element through volatilization.

When the presence of a small amount of carbon in the ferrovanadium is not objectionable, reduction by carbon in the electric furnace is employed.[3] The ore used may be the vanadate of iron or calcium or the oxides of vanadium. Roasted patronite is sometimes reduced directly in the electric furnace by the use of lime to remove the sulfur. This process is difficult to carry out, requires an excess of carbon, and its large-scale operation has only recently been accomplished. A very high temperature must be used also and the reduction must be completed in a short time. But by using a high voltage, high current density, and close spacing of the electrodes and then

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[1] *Zeit. Elektrochem.* **9** 831 (1903).

[2] *Min. Ind.* 1919.

[3] See R. S. Anderson, *Trans. Am. Electrochem. Soc.*, **37** 277 (1920), and B. D. Saklatwalla, *ibid.* **37** 341.

feeding the ore directly into the heat zone[1] good results are obtained. Considerable carbon is retained by the ferrovanadium, a part of which is removed by fusion with either an oxide of iron or an oxide of vanadium. The final product contains from 1.5 to 6 per cent carbon, which is a matter of serious consequence in the steel industry, because the vanadium combines with the carbon, forming a stable carbide which dissolves in the steel without decomposition, so the beneficial influence of vanadium is not produced. The electric reduction takes place mainly at Bridgeville, Pennsylvania, where the thermite reduction process has been in use for some time. Recently an electric furnace capable of producing about 75,000 pounds of alloy per month was installed for treating the slag from the thermite process dump. Early in 1920 production of ferrovanadium in the electric furnace was begun at York, Pennsylvania.

Several patents have been issued for the production of ferrovanadium in an electric furnace, using silicon as a reducing agent. The process produces a high temperature and hence is successful. The product, however, contains some silicon.

The vanadium industry has grown very rapidly within recent years. It is said that in 1906 the total ferrovanadium produced did not exceed \$50,000 in value. But five years later it amounted to \$1,500,000. During the World War the enormous demand for vanadium steel greatly stimulated production and the output increased at an astonishing rate. During 1920 the total production of the vanadium industry probably exceeded 4,000,000 pounds[2] of V_2O_5. Practically all the vanadium produced in the world is under the control of the Vanadium Corporation of America.

During the latter part of 1918 ferrovanadium sold for \$5 per pound of contained vanadium. During 1919 the demand was strong, and the price rose to \$7 or more per pound for the alloy low in both carbon and silicon. The demand was so strong that the alloy with a high carbon and silicon content sold freely, and for the first time purchasers of carnotite were compelled to pay for the vanadium which it contained. During the latter part of 1920 the market became dull, possibly due to

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[1] See *Pat.* 1,435,742; *Chem. and Met. Eng.* **27** 1232 (1922).

[2] R. B. Moore, *Eng. and Min. Jour.* **111** 152 (1921).

the general business depression along with the active production of recent months. The Chemical Products Company of Denver, Colorado, who have been producing vanadium and radium announced the indefinite suspension of activities because of the poor market for vanadium.[1]

Properties. — Vanadium prepared by the reduction with hydrogen is a light gray powder, from which a crystalline mass may be obtained which possesses a brilliant silver-white luster. The metal takes a splendid polish, which is not tarnished by exposure to air. It has a specific gravity of 5.68 and is harder than steel or quartz. It may be heated in hydrogen to redness without fusing or vaporizing. It is non-magnetic. When the compact form of the metal is heated in the air it is oxidized, showing various colors as the oxidation progresses: brown (V_2O), gray (V_2O_2), black (V_2O_3), blue (V_2O_4), and red (V_2O_5). When the powdered metal is thrown into a flame or heated in oxygen it burns with brilliant scintillations. When heated in an atmosphere of chlorine it combines directly with it, forming VCl_4; at high temperatures it also combines directly with nitrogen, forming VN, and with carbon, probably forming VC. It is not soluble in hydrochloric acid nor in dilute sulfuric acid, but dissolves in nitric, hydrofluoric, and strong sulfuric acids. Solutions of the alkalies have little effect upon it, but with fused alkaline reagents it reacts readily, forming water-soluble vanadates and liberating hydrogen.

It alloys with iron and aluminium.

Uses. — The greatest uses of vanadium are in connection with the preparation of special grades of steel. The effect of adding vanadium is twofold: (1) it acts as a scavenger, being especially efficient for the removal of nitrogen and oxygen; (2) a small per cent remains in the steel, passing into solid solution in the ferrite, making the metal more coherent and imparting increased toughness and tensile strength.

As a scavenger its efficiency depends upon its ability to unite with nitrides and oxides and carry them into the slag. It is more efficient for this purpose than ferrosilicon and ferromanganese. Consequently it is added after these alloys have produced the best results of which they are capable. Vanadium has accomplished surprising results in improving the quality

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[1] *Chem. and Met. Eng.* **24** 491 (Mar. 16, 1921).

of crucible and open hearth steel, but it is used also for Bessemer and even in cast iron. It is usually added as small lumps or as a powder to the ladle as the steel is being drawn. Usually little difficulty is encountered in obtaining a satisfactory mix. The melting point of ferrovanadium containing 30–35 per cent vanadium is 1425°, but the melting point rises as the amount of vanadium is either increased or decreased beyond these limits. For use at moderate temperatures an alloy of this composition is preferred. The quantity added depends upon the amount of scavenging which it is expected to accomplish, but only a small amount is needed as a permanent constituent of the steel. For case hardening material 0.12–0.14 per cent is sufficient; for axles, shafts, saws, dies, etc., 0.16–0.2 per cent is used; springs usually require a little more; armor plate, gun shields, etc., contain 0.3–0.4 per cent and high speed steel contains 0.35–0.5 per cent. For the latter purpose as much as 2 per cent vanadium is sometimes used, but for general purposes the amount does not exceed 0.3 per cent. Vanadium steels are less porous, and will withstand strain, vibration, and shock very successfully. The effect upon high speed steel is much the same as chromium, since it increases the hardness and red hardness of the cutting edge, and imparts greater durability to the tool.

In modern steel making, vanadium is generally used in connection with other alloying elements. Typical of these are the chrome-vanadium steels, which are generally made in the open hearth furnace, the alloying metals being added a short time before the casting is made. This variety of steel is used commonly for making automobile parts, where it is valued, not only on account of its toughness and strength, but because it is particularly free from surface imperfections. It resembles chrome-nickel steel in physical properties and is able to compete with the cheaper nickel because the latter acts only as an alloying element and not as a scavenger.

In cast iron the amount of vanadium varies from 0.08 to 0.15 per cent. Its function is that of a scavenger, and its beneficial results are almost wholly indirect. It causes a more even distribution of the carbon, lessens porosity and brittleness, and checks spalling and flaking. The strength of the casting is increased 10–25 per cent by 0.1 per cent of vanadium. It is claimed that the decrease in the number of rejected castings more than compensates for the increased cost of the vanadium treatment.

Vanadium forms alloys with other metals, some of which are of considerable commercial interest. The aluminium alloys containing 10 per cent or less of vanadium are malleable, while those containing 20–25 per cent vanadium may be pulverized in water. The alloy of the composition AlV is the hardest one of the series. A copper-vanadium alloy containing 10–15 per cent vanadium, 60–70 per cent copper, 10–15 per cent aluminium, and 2–3 per cent nickel is prepared and used for the production of solid copper castings and bronzes and in the manufacture of aluminium alloys. Approximately 100 tons of cupro-vanadium are sold annually to brass and bronze makers.[1] Vanadium is also used to harden gold for use in dentistry.

The compounds of vanadium find a wide variety of applications, but none of these use more than a very small amount of the element. For many years vanadium salts have been used in photography, where they are serviceable for the production of a green color on bromide prints. One plan uses a mixture of vanadium tetrachloride, oxalic acid, ferric oxalate, and potassium ferricyanide.[2] A plan for using vanadium or its alloys in place of lead and vanadium salts in place of sulfuric acid in storage batteries is covered by French patent 357,601 (1905). Writing inks are made by mixing vanadium salts with tincture of galls. These inks produce a deep black color, which is unaffected by chlorine, acids, or alkalies, but it fades gradually and accordingly has not won great popularity. In the textile industries, vanadium compounds are used as mordants in the dyeing and printing of cotton and especially in fixing aniline on silk. Ammonium vanadate has been used in the dyeing of leather. In ceramics the colored compounds are used to produce certain colors in both glass and pottery, while V_2O_5 or HVO_3 is serviceable as a gold bronze. The oxides of vanadium not only serve as oxidizing agents, but they are efficient catalysts, serviceable in the oxidation of certain organic compounds,[3] such as the oxidation of sugar to oxalic acid or

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[1] Thomas, *Raw Material*, **4** 167 (1921); also *Chem. and Met. Eng.* **27** 1185 (1922).

[2] L. Lumiere, *Moniteur Scientifique* **42** 437 (1894); and *German Pat.* 215,017 (1909); and *U. S. Pat.* 979,887 (1910).

[3] *French Pat.* 345,701 (1904); *Jour. prakt. Chem.* **75** 146 (1907).

alcohol to aldehyde by the air. A small amount of vanadium added to rubber increases its density, decreases its porosity, and doubles its tensile strength. Rubber so treated is oil- and waterproof. Vanadium carbide has been tried as a filament for incandescent lamps. Vanadium salve is recommended for burns, and the pentoxide has a limited use in medicine in treating tuberculosis and diseases due to defective metabolism. The physiological effect of vanadium is somewhat doubtful. The compounds are usually considered as poisonous,[1] an affliction called vanadiumism being caused by exposure to fumes of V_2O_5. The manager of a large vanadium-producing plant questions the idea that vanadium is poisonous in a manner similar to lead, since workmen in his plant who have been exposed to vanadium dust for five years show no sign of poisoning.[2] It is also claimed that there is no well defined case of vanadium poisoning shown in the literature. Vanadium driers for linseed oil may be prepared by heating ammonium vanadate with rosin or linseed oil.[3] This drier produces a smooth, tough film, but there is also some darkening of the oil.

Compounds. Vanadium forms a great variety of compounds. It is known in five conditions of oxidation as represented by its five oxides, all of which are represented by salts except the suboxide V_2O. There is also much confusion concerning the names of these various classes of compounds due to the fact that in the older literature a different system of nomenclature was employed. Table XXXI attempts to classify the various compounds and to show the relationship between the different classes. In addition to the classes shown in the table, vanadium forms many complex compounds, such as the polyvanadates and those in which V_2O_5 condenses with such oxides as P_2O_5, MoO_3, WO_3, SiO_2, As_2O_5, etc. In the vanadyl compounds the radical VO displays valences of 1, 2, or 3, forming respectively such compounds as the monochloride, VOCl, the dichloride, $VOCl_2$, and the trichloride, $VOCl_3$. The divanadyl radical V_2O_2 also displays varying valence, though in the most common derivatives of this class it is quadrivalent, as in divanadyl tetrachloride, $V_2O_2Cl_4$.

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[1] *Eng. and Min. Jour.* **92** 24; *Jour. Am. Med. Assoc.*, June 3, 1911.

[2] *Eng. and Min. Jour.* **92** 92.

[3] Rhodes and Chen, *Jour. Ind. and Eng. Chem.* **14** 222 (1922).

TABLE XXXI

Compounds of Vanadium

VALENCE	OXIDE	NATURE	TYPICAL SALTS	CHARACTERISTIC COLOR	FORMER NAME	PRESENT NAME	IMPORTANCE
V^{I}	V_2O	Basic	None	———	Lacking	Hypovanadious	Very slight
V^{II}	$VO(V_2O_2)$	Basic	VCl_2, V_2S_2 VSO_4	Lavender	Hypovanadious	Vanadious	Not great
V^{III}	V_2O_3	Basic	VCl_3, $VOCl$, V_2S_3 VN, $V_2(SO_4)_3 \cdot K_2SO_4 \cdot 24\,H_2O$	Green	Vanadious	Vanadic	Greater than preceding
V^{IV}	$VO_2(V_2O_4)$	Basic	VCl_4, $VOCl_2$ VBr_4, $VOBr_2$	Blue		Tetrachloride, Vanadyl	Of some importance
		Feebly acidic	$Na_2V_4O_9$	Brown to black	Hypovanadates	Vanadites	
V^{V}	V_2O_5	Feebly basic	V_2S_5, $VOBr_3$	Orange or yellow			Very slight
		Strongly acidic	$NaVO_3$	Pale yellow		Metavanadates	Most important
			$Na_4V_2O_7$			Pyrovanadates	Not common
			Na_3VO_4	Yellow		Orthovanadates	Very important

Vanadium pentoxide or vanadic anhydride, V_2O_5, is the most important oxide, because from it nearly all the vanadium compounds are derived. It is usually prepared by heating ammonium metavanadate, NH_4VO_3, which is one of the forms in which vanadium comes on the market. It crystallizes in beautiful yellowish red rhombic prisms, which are difficultly soluble in water. The water solution has an acid reaction and reacts with alkalies forming stable vanadates. The anhydride also dissolves in strong acids, forming pentavalent salts.

Three classes of vanadates are formed corresponding to the phosphates. The order of stability in water solution is the reverse of that shown by the phosphates, the metavanadates being the most stable. Consequently these are the most common vanadates obtained in solution. The other vanadates are, however, the most stable at elevated temperatures, so these usually result from alkaline fusions.

Metavanadic acid, HVO_3, is prepared by boiling copper vanadate with nitric acid. It is an unstable, brown precipitate resembling $Fe(OH)_3$ in appearance. The alkaline pyrovanadates are soluble in water, but the salts of the heavy metals are mostly insoluble.

Orthovanadic acid, H_3VO_4, is unknown, but its salts are obtained by fusion. The alkaline orthovanadates are soluble in water, while the salts of the heavy metals are obtained by precipitation. Orthovanadate solutions are hydrolyzed; as, for example, $2\,Na_3VO_4 + H_2O = Na_4V_2O_7 + 2\,NaOH$.

In addition to these series, V_2O_5 is the anhydride of many others, such as the tetravanadates, like $(NH_4)_2V_4O_{11} \cdot 4\,H_2O$, the hexavanadates, like $Na_2H_2V_6O_{17}$, etc. Pervanadic acid, HVO_4, is formed when V_2O_5 is added to hydrogen peroxide in the presence of sulfuric acid.

Vanadium dioxide, VO_2 (or tetroxide, V_2O_4), may be prepared either by partial reduction of the pentoxide or by oxidizing VO in the air. It is soluble in acids, forming solutions of vanadyl salts, which have a bright blue color. In the presence of alkalies vanadites are formed, all of which are insoluble except those of the alkali metals. The quadrivalent divanadyl compounds may be considered derivatives of this oxide, the most important compounds of this class being divanadyl tetrachloride, $V_2O_2Cl_4$, and divanadyl sulfate, $V_2O_2(SO_4)_2$.

Vanadium sesquioxide or trioxide, V_2O_3, is formed by the reduction of V_2O_5 with carbon or hydrogen. It is a black powder with some metallic properties. It takes up oxygen from the air, forming VO_2, and is oxidized by chlorine, giving $VOCl_3$ and V_2O_5. The sesquioxide is difficultly soluble in acids, vanadic salts being formed by other methods. The best-known salt of this class is the sulfate, which forms a greenish violet potash alum and a ruby-red caesium alum.

Vanadium monoxide, VO (or V_2O_2), is one of the substances which Berzelius mistook for the element vanadium. It is prepared by the vigorous reduction of V_2O_5 or $VOCl_3$. It is a gray powder with some metallic luster, brittle, difficultly fusible, and a fairly good conductor of electricity. It burns in the air, forming V_2O_5 and in chlorine, giving $VOCl_3$. It is insoluble in water, but dissolves in acids yielding vanadous salts, of which the sulfate, VSO_4, is most interesting. It absorbs oxygen so readily that it bleaches indigo as quickly as chlorine. A neutral lavender vanadious solution is as delicate a test for free oxygen as alkaline pyrogallate, since it quickly becomes dark brown because of the absorption of oxygen. The oxide is sufficiently stable to permit it to enter into combination as a radical, forming such compounds as vanadyl mono-, di-, and tri-chloride.

Vanadium suboxide, V_2O, forms as a brown coating when metallic vanadium is exposed to the air at ordinary temperatures. At higher temperatures it is transformed to the other oxides. It forms no salts.

Nitrogen forms two vanadium compounds, VN and VN_2. The former is the stable, metallic-appearing powder which Berzelius sometimes obtained when he was attempting to prepare the metal.

Fluorine forms $VF_3 \cdot 3\,H_2O$ and VOF_2, besides a very large number of double and acid fluorides.

Chlorine forms the simple chlorides, VCl_4, VCl_3, and VCl_2, and the oxychlorides, $VOCl_3$, $VOCl_2$, VOCl, $V_2O_2Cl_4 \cdot 5\,H_2O$, V_2O_2Cl, and $V_2O_3Cl_2 \cdot 4\,H_2O$.

The tetrachloride, VCl_4, is formed when the vapor of $VOCl_3$ is mixed with chlorine and passed over red-hot charcoal. It is a dark reddish brown liquid which fumes in moist air and is decomposed by water. It has a specific gravity of 1.85 and boils at 154°. At ordinary temperatures it slowly decomposes, yielding VCl_3 and chlorine; this reaction proceeds more rapidly at the boiling temperature or in strong light.

The trichloride, VCl_3, is formed by the decomposition of the tetrachloride or by heating V_2S_3 in chlorine. It forms pinkish, shining tablets, resembling $CrCl_3$ in appearance, which are extremely hygroscopic. It is non-volatile, but when heated with hydrogen it first loses a third of its chlorine, forming VCl_2 and later all, leaving the metal. It forms a hydrate $VCl_3 \cdot 6\,H_2O$ and sparingly soluble double alkali chlorides, such as $VCl_3 \cdot 2\,KCl \cdot H_2O$.

The dichloride, vanadious chloride, VCl_2, is made by reducing VCl_4 with hydrogen. It forms fine light green crystals which are exceedingly deliquescent and yield a lavender solution, which has marked bleaching properties and is a more powerful reducing agent than chromous chloride.

Vanadyl trichloride, $VOCl_3$, is a greenish yellow mobile liquid prepared by the action of chlorine on the oxides VO and V_2O_3 or by reducing V_2O_5 in an atmosphere of chlorine. It fumes in moist air, and when a small amount of water is added it turns blood red due to the formation of vanadic acid by hydrolysis; but on further dilution the vanadic acid dissolves, giving a clear yellow solution. When reduced, it yields vanadyl dichloride, $VOCl_2$, green tablets, deliquescent; vanadyl monochloride, VOCl, brown powder, insoluble in water; and divanadyl monochloride, yellow crystalline powder.

Bromine and iodine form compounds similar to the chlorine derivatives.

Carbon reduces V_2O_5 in the electric furnace and unites directly with the metallic vanadium, forming VC, which forms very hard silvery white crystals. They melt at 2750° and burn in oxygen.

Vanadium forms a number of complex cyanides and sulfocyanides such as $K_3V(CN)_6$, $K_4V(CN)_6 \cdot 3H_2O$ and $3KCNS \cdot V(CNS)_3 \cdot 4H_2O$. Vanadyl derivatives of this sort have also been prepared.[1]

Silicon forms two silicides, V_2Si and VSi_2, both by heating V_2O_5 with silicon in the electric furnace. Both compounds are hard and sparingly soluble in acids except hydrofluoric.

Sulfur forms compounds analogous to the oxides. The most stable compound is V_2S_3, which is prepared by heating any of the oxides, chlorides, or oxychlorides in a stream of H_2S. Reduction of V_2S_3 gives VS, and heating with sulfur produces V_2S_5.

Vanadium sulfate, $VSO_4 \cdot 7H_2O$, is prepared by reducing V_2O_5 in the presence of sulfuric acid first by sulfur dioxide to a blue solution and then electrolytically to a violet color. Air must be carefully excluded. By evaporating this solution in a vacuum, [illegible] violet crystals are obtained. They are readily soluble in water and the solution readily reduces salts of copper, silver, gold, tin, platinum, and mercury to the metallic state.

Vanadic sulfate, $V_2(SO_4)_3$, forms as a finely crystalline yellow powder when V_2O_5 in sulfuric acid is reduced electrolytically till the vanadium is in the trivalent condition, then is heated in an atmosphere of carbon dioxide. It is a vigorous reducing agent, precipitating copper from an acid solution of $CuSO_4$. Alums with ammonium, potassium, rubidium, caesium, and thallium have been prepared by electrolytic reduction of the metavanadate and evaporation in the presence of the desired alkali sulfate.

Vanadyl sulfates may be prepared by reducing V_2O_5 in sulfuric acid or by dissolving other oxides of vanadium in sulfuric acid. Many double salts and both acid and basic salts of these compounds have been prepared.

Detection. Vanadium may be separated from phosphorus by reducing vanadic acid with sulfur dioxide or by adding ammonium citrate to the strongly acid solution. Phosphoric acid may then be precipitated with ammonium molybdate, the vanadyl compounds remaining in solution.

Vanadium may be separated from aluminum and iron by fusing with sodium carbonate, leaching with water containing a little Na_2CO_3, then filter and boil the filtrate with NH_4NO_3. Filter again and acidify the filtrate with HCl, neutralize with NH_4OH, bring to a boil, and add $BaCl_2$. This method may be made quantitative, the first precipitate being $Fe(OH)_3$, the second $Al(OH)_3$, and the final precipitate $Ba(VO_3)_2$.

Vanadium may be separated from uranium and chromium as follows:[3] Make the solution faintly alkaline with ammonia, then faintly acid with acetic acid, add ammonium phosphate and precipitate the uranium as phosphate. Reduce the filtrate with SO_2, boil, and add bromine, oxidizing vanadium but not the chromium. Add a faint excess of ammonia, precipitating chromium completely. Make the filtrate alkaline with ammonia, and saturate with H_2S, precipitating the oxysulfide of vanadium, pink or violet.

Vanadium may be separated from arsenic by reducing the vanadium with sulfur dioxide and then precipitating the arsenic with H_2S, or by

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[1] *Zeit. anorg. Chem.* **36** 281 (1903).

[2] *Helvetica Chim. Acta* **8** 550.

[3] Browning, *Jour. Am. Chem. Soc.* **43** 114 (1921).

heating the mixed sulfides in hydrogen chloride, the volatile arsenic chloride distilling away at 130°; or by distilling off the arsenic in a methyl alcohol solution.[1]

Vanadium may be separated from molybdenum and tungsten by the precipitation of ammonium metavanadate by adding an excess of ammonium chloride to a solution containing an alkali vanadate, molybdate, and tungstate.

On account of the large number of colored compounds formed by vanadium, a great many color tests have been suggested for the identification of this element. Some of these are as follows: —

(1) If vanadium sulfide is dissolved in 5–100 cc. of dilute nitric acid and a few drops of 3 per cent. H_2O_2 are added, pervanadic acid, HVO_4, is formed, recognizable by its orange to red color.

(2) Reducing agents produce a successive change in colors — V_2O_5 red, VO_2 blue, V_2O_3 black, VO gray, V gray.

(3) Ammonium chloride added to a neutral or alkaline solution of a vanadate precipitates NH_4VO_3 colorless, yielding red V_2O_5 on ignition.

(4) If a crystal of strychnine sulfate is added to a drop of strong sulfuric acid and then a drop of a vanadium solution is added, color changes from violet to rose are observed.

(5) A vanadium borax bead is colorless or yellow (depending on the amount of vanadium present) in the outer flame, and green or brown in the inner, becoming green on cooling.

(6) A delicate reagent for detecting vanadium in small amounts is prepared by warming 0.2 g. diphenylamine in 100 cc. water. Cool and filter. Add 1 cc. concentrated HCl and 1 cc. of this reagent to a dilute vanadium solution and shake. A violet color appears slowly, the time required and the intensity depending on the amount of vanadium.[2]

A field test which is reliable for almost all vanadium minerals is the development of a rich red solution when treated with concentrated hydrochloric acid. In case of the silicate ores the color develops slowly or on warming. On careful dilution a green color appears for a short time. If the solutions are not too dilute hydrogen peroxide causes the color to reappear.

Estimation.[3] — The quantitative determination of vanadium is complicated, the procedure used depending largely on the amount and nature of the accompanying substances. The following brief outlines are suggestive: —

Gravimetrically, vanadium is usually weighed as the pentoxide. This may be obtained by igniting the ammonium metavanadate, or mercury vanadate or vanadic acid. Cupferron is a popular and efficient precipitant.[4]

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[1] Moser and Ehrlich, *Ber.* **55 B** 430 (1922).

[2] *Anales soc. quim. Argentina*, **5** 185 (1917).

[3] See *Bull.* 70, U. S. Geol. Surv., p. 90; W. F. Bleecker, *Chem. and Met. Eng.* **9** 209 (1911); W. W. Clarke, *Chem. and Met.* **11** 91 (1913); J. Kent Smith, *Eng. and Min. Jour.* **93** 1094 (1912); Misson, *Bull. soc. chim. Belg.* **31** 123 (1922); Schaal, *Jour. Ind. and Eng. Chem.* **13** 698 (1921).

[4] *Am. Jour. Sci.* **41** 389; *Jour. Ind. and Eng. Chem.* **12** 350 (1920).

Volumetric methods depend on the reduction of [illegible] state, then reoxidation. The reduction may be [illegible] II, tartaric, oxalic, or citric acid, or [illegible] be brought about by permanganate, [illegible] tails the original articles[1] should be consulted. [illegible] tial reduction vanadium and molybdenum may [illegible] same solution;[2] in a similar manner vanadium and [illegible][3] Electrometric titration of vanadium with [illegible] may be carried out[4] and colorimetric methods [illegible][5]

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[1] Hillebrand, *Jour. Am. Chem. Soc.* **20** [illegible] *Sci.* **15** (4) 389; Gooch and Stookey, *ibid.* **14** [illegible] **17** (4) 4; Browning, *ibid.* **11** (4) [illegible] and Browning [illegible] **7** [illegible] McCay and Anderson, *Jour. Am. Chem. Soc.* **44** [illegible]

[2] See Edgar, *Am. Jour. Sci.* **25** 332 [illegible]

[3] *Ibid.* **26** 79 (1908). For other methods see [illegible] *Met.* **17** [illegible] *Chem. Analyst.* **29** 19 (1920); and *Jour. Ind. and Eng. Chem.* **11** [illegible]

[4] Kelley and others, *ibid.* **13** 939 [illegible] *Jour. Am. Chem. Soc.* **44** 2750 (1922) [illegible] **45** [illegible]

[5] Kruft, *Zeit. angew. Chem.* **35** 300 (1922).

CHAPTER XIII

GROUP V — COLUMBIUM AND TANTALUM

Historical. — In 1801, an English chemist, Hatchett, studied a black mineral which had found its way from the Connecticut valley to the British Museum. The mineral was found to be composed largely of iron, but it contained a small per cent of another element which possessed new properties. It was described as forming "a white tasteless earth, insoluble in hot and cold water, acid to litmus, infusible before the blowpipe, and not dissolved by borax." Hatchett believed he had discovered a new element and suggested the name columbium, since the mineral from which it was extracted came from America.

In 1802, Ekeberg, in Sweden, studied a mineral from Finland and found in it an element which resembled tin, tungsten, and titanium, but differed essentially from each. He proposed the name tantalum for the new element, because its characteristic insolubility in acids suggested the familiar Greek myth regarding Tantalus, since the substance "when placed in the midst of acids is incapable of taking any of them up."

The similarity shown by Hatchett's columbium and Ekeberg's tantalum attracted attention, and in 1809 Wollaston attempted to prove[1] that the two elements were identical. He prepared a list of similar properties shown by the acids of the elements, and claimed that the greatest difference was the specific gravity of the minerals — tantalite having a specific gravity of 7.95 and columbite 5.91. This difference he explained as due either to different conditions of oxidation or to different states of molecular structure. His deductions were accepted, and for many years the "element" was called either tantalum or columbium.

In 1839, Wöhler showed[2] that the acid obtained from Bavarian tantalite had strange properties. In 1844, Rose concluded[3] that certain columbites yielded two distinct acids, one of which resembled the acid prepared from tantalite and another which differed in properties. He considered the latter a new element and suggested the name niobium from Niobe, daughter of Tantalus. The individuality of the two elements was gradually developed by Hermann, Blomstrand, and Marignac, but the final step in the proof came in 1865 when Deville and Troost determined[4] the formulas of certain columbium and tantalum compounds by vapor density methods. Columbium and niobium were found to be the same element. The name niobium is commonly used in Germany, but in England and

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[1] *Phil. Trans.* **92** 49 (1802).
[2] *Pogg. Ann.* **43** 91 (1839).
[3] *Ibid.* **63** 307, 693 (1844); also **69** 118 (1846).
[4] *Compt. rend.* **60** 1221 (1865).

the United States the name columbium [illegible] An important event in the development [illegible] J. Lawrence Smith of [illegible] samarskite.[1]

Occurrence. — The elements columbium and tantalum are found in many rare minerals widely distributed over the earth's surface. There are few deposits which are extensive enough to be of any commercial significance. Almost always the elements are found in intimate mixture as columbates and tantalates. For example, the mineral columbite passes by insensible gradations from its normal composition $Fe(CbO_3)_2$ to that of nearly pure tantalite $Fe(TaO_3)_2$. Manganese sometimes replaces part of the iron, while tin and tungsten are frequent minor components, but a rather loose custom prevails of calling any given sample either columbite or tantalite, depending on the element which predominates. The specific gravity increases quite uniformly as the per cent of tantalum increases, so the composition of any sample may be roughly inferred from its relative weight. Occasionally, however, minerals are found in which only traces of one of the elements are found. A few of the principal minerals are as follows:

		Per Cent Cb_2O_5	Per Cent Ta_2O_5
Columbite	$Fe(CbO_3)_2$	82.7	
Tantalite	$Fe(TaO_3)_2$		86.1
Pyrochlore	$R(CbO_3)_2 \cdot R(Ti,Th)O_3$	47.13–53.19	
Fergusonite	$(Y, Er, Ce)(Cb, Ta)O_4$	14–46	4–43
Samarskite	$(Fe, Ca, UO_2)_3(Ce, Y, etc.)_2(Cb, Ta)_6O_{21}$	41–56	14–27
Euxenite	$R''(CbO_3)_2 \cdot R_2'''(TiO_3)_3 \cdot \frac{3}{2}H_2O$	18–35	
Polycrase	$R''(CbO_3)_2 \cdot 2R_2'''(TiO_3)_3 \cdot 3H_2O$	19–25	1–4

The ores are mined chiefly for their tantalum content, since there is now no demand for columbium or its compounds. The most important ores come from Australia, where the amount of Ta_2O_5 runs from 50 to 70 per cent. In the United States some tantalum material has been obtained in Connecticut and in the Black Hills of South Dakota, but the American ore scarcely ever exceeds 40 per cent Ta_2O_5 and may run as low as

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[1] *Nature*, 21 146 (1879); see also *Bull.* No. 74, U. S. Geol. Survey, 1891.

10 per cent. Tantalum ores are also found in Finland, Sweden, Norway, Russia, Bavaria, Italy, and Malay; also, in Maine, Massachusetts, New York, Pennsylvania, Virginia, North Carolina, Colorado, and California. The demand for tantalum is relatively slight and irregular, so most of these deposits are undeveloped. The production from all sources is subject to great fluctuation. In 1907, Australia produced ore valued at £327, but in the years 1910–13 no production is recorded. The amount produced in the United States is so small that it is not reported among other mineral resources of the country.

The price of tantalite quoted in March, 1917, was $250 per ton of ore guaranteed to contain at least 35 per cent of combined columbic and tantalic oxides. Material containing 65 per cent Ta_2O_5 was quoted at $15 per unit, which is equivalent to $975 per ton.

Extraction.[1] — Columbium and tantalum are extracted from their ores by fusion methods, since their salts are characterized by insolubility in acids. Hydrofluoric acid is used as a solvent for these elements in a few special cases. The following methods have been used: —

(*a*) A high-grade ore containing little titanium is fused in a nickel or silver crucible with six times its weight of KOH. After cooling, the melt is dissolved in water, HCl is added, and the extract boiled for 20 minutes. The oxides of columbium and tantalum, mixed with varying amounts of tungsten, tin, and silica are filtered off and purified.

(*b*) Bisulfate fusion in a platinum or quartz crucible is recommended for minerals containing a small amount of columbium and tantalum, especially the complex minerals such as the titanocolumbates and -tantalates. The mineral is added to 10 times its weight of $NaHSO_4$ and fusion continued until disintegration is complete. After cooling, the cake is extracted with a large volume of acidulated water, and the residue digested with ammonium sulfide to remove tin and tungsten. To remove silica and titanic acid evaporate with HF and H_2SO_4, pour the mass into water, nearly neutralize with ammonia, and boil 3–4 hours with salicylic acid. The precipitate is fairly pure Cb_2O_5 and Ta_2O_5.

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[1] See Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*, p. 138.

(*c*) Fusion with three parts of potassium fluoride quickly disintegrates the finely pulverized ore. Grind the melt, extract with water containing HF, and evaporate. K_2TaF_7 crystallizes first in fine needles and on further concentration $2\,KF \cdot CbOF_3 \cdot H_2O$ crystallizes in large flat plates.

(*d*) Fusion with Na_2O_2 is effective and rapid. The method is similar to (*a*).

(*e*) Fusion with K_2CO_3 is similar to (*a*), but the salt is less fusible and so the method is accordingly less convenient.

Separation. Columbium and tantalum extracted by almost any method may contain such impurities as tin, tungsten, silica, titanium, zirconium, or antimony.

Tin or antimony may be removed by digesting the precipitated acids with yellow ammonium sulfide.

Tungsten is extracted by digestion with dilute ammonia or ammonium carbonate; or by digesting with warm one per cent NaOH and boiling with an excess of NH_4NO_3.

Silica is removed with HF and H_2SO_4.

Titanium may be separated quantitatively by adding an excess of salicylic acid and boiling in a reflux condenser for 3–4 hours. The titanium is found in the yellow filtrate from which it may be precipitated by ammonia.

Zirconium is separated by fusion with bisulfate, the melt being extracted with dilute sulfuric acid. The zirconium sulfate dissolves.

The separation of columbium and tantalum from each other can best be accomplished by fractional crystallization. The original method of Marignac[1] consisted in adding to the mixed fluorides enough KF to form the double salts. The solution is then evaporated partly, and on cooling needle-like crystals of K_2TaF_7 separate out. On further evaporation broad plates of $2\,KF \cdot CbOF_3 \cdot H_2O$ are deposited. Potassium fluotantalate is soluble in 151–157 parts of cold water, and potassium columbium oxy-fluoride is soluble in 12–13 parts of cold water. Four or five precipitations with KF will yield pure K_2TaF_7 uncontaminated by columbium.

After the first crystals of K_2TaF_7 have separated out, it is customary to evaporate the remaining solution to dryness, and ignite for several hours at a low temperature. In this way the

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[1] *Ann. Chim. Phys.* **8** 5, 49 (1866).

remaining tantalum is rendered insoluble. The ignited residue is moistened with strong hydrofluoric acid, taken up with water, and the process repeated until tantalum is all removed. This method is useful for removing a small amount of tantalum from columbium material.

A modification[1] of Marignac's method adds a saturated solution of KCl in place of KF, the separation being accomplished in the same manner.

Iron and manganese form compounds which are isomorphous with K_2TaF_7 and are therefore not removed by Marignac's method. One method of separating these elements is to decompose the fluorides with concentrated HCl, add HF, and then NH_4F when the manganese and iron are precipitated.

A mixture of the oxides of columbium and tantalum may be separated by digesting with a 1 : 1 mixture of selenium oxychloride and concentrated sulfuric acid. The columbium dissolves, leaving the tantalum unaffected. This treatment may be made quantitative by repeating the process several times, but if titanium is present it is extracted along with the columbium.[2]

Metallurgy. — Columbium may be prepared in the metallic state in several ways:

(1) Blomstrand first prepared the metal[3] in 1866 by the reduction of the chloride with hydrogen. A mirror-like deposit which doubtless contains the hydride forms in the tube.

(2) Somewhat more pure columbium may be obtained by passing a mixture of $CbCl_4$ vapor and hydrogen through a hot tube.

(3) Reduction by the thermit process yields a product containing about three per cent aluminium, but this metal may be removed by heating the alloy *in vacuo*.[4]

(4) Electrolysis of a solution of potassium fluoxy-columbate.

(5) Reduction of the oxide with misch metal.

(6) A mixture of CbO_2 and paraffin may be pressed into threads and reduced by the heating effect of an alternate current in a vacuum.

Tantalum was first prepared by Berzelius and Rose, who heated potassium fluotantalate in a crucible with metallic potas-

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[1] Malmberg and Winzer, *Zeit. angew. Chem.* **26** 157 (1913).

[2] H. B. Merrill, *Jour. Am. Chem. Soc.* **43** 2378 (1921).

[3] *Jour. pr. Chem.* **97** 37 (1866).

[4] Von Bolton, *Zeit. Elektrochem.* **13** 145 (1907).

sium and washed out the potassium fluoride with water and nitric acid. Recently a similar method has been proposed by which sodium fluotantalate is reduced with sodium.[1]

Moissan[2] reduced Ta_2O_5 with carbon in an electric furnace, but the product contained both oxide and carbide. The oxide has also been reduced with misch metal and by molding into rods with paraffin and heating in a vacuum by an alternating current.

An English patent (1906) describes the production of pure tantalum by electrolysis of fused K_2TaF_7 in a refractory crucible of magnesium oxide or tantalum oxide, using pure tantalum metal as cathode and the impure metal as anode. A French patent (1907) claims that very pure tantalum may be prepared by electrolysis of tantalum material in a 3 per cent solution of H_2SO_4. The electrodes are platinum or carbon and a current of 0.1–0.3 ampere at two volts is required.

All of these methods produce a relatively impure metal, usually in powder form, which may be purified by thorough extraction with water and strong acids. The powder may then be pressed into bars, subjected to heat treatment and final fusion in a vacuum furnace. The high temperature required for fusion aids in eliminating any residual impurities. The metal is now prepared in commercial quantities with a purity of at least 99.5 per cent.[3]

Properties. — Metallic columbium has a steel-gray color and a brilliant metallic luster. Its hardness compares with that of wrought iron, but it is lighter in weight, more easily fusible, and softer than tantalum. It is malleable, ductile, and it can be welded at red heat. In the powder form columbium oxidizes rapidly in the air, but the compact form is more resistant, probably due to the formation of a protective coating of oxide. When heated in the air it combines slowly with oxygen, forming Cb_2O_4. It combines with hydrogen, forming CbH, a metallic-appearing solid which resists the action of acids, but burns in the air. At 1200° it combines with nitrogen and with chlorine at red heat. It is unattacked by hydrochloric or nitric acids or by a mixture of the two; hydrofluoric acid dissolves it to some extent; a mixture of nitric and hydrofluoric acids is a fairly

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[1] *Mining Jour.* **80** 363 (1906).

[2] *Compt. rend.* **134** 211 (1902).

[3] C. W. Balke, *Chem. and Met. Eng.* **27** 1271 (1922).

good solvent, and it reacts readily with fused alkalies and fused oxidizing agents.

Tantalum resembles platinum in appearance, being somewhat darker in color. Its melting point[1] is the highest of any metal except tungsten. The worked metal has a specific gravity of 16.6. The pure metal is remarkably ductile and malleable and possesses great toughness. The tensile strength is very high, a fine wire giving a breaking strength of 93 Kg. per square millimeter, more than copper, nickel, or platinum, but less than molybdenum or tungsten. Tantalum may be drawn into wire a few mils in diameter without intermediate annealing, although the metal is subject to strain hardening, like copper and silver. Tantalum, however, resembles tungsten and molybdenum in permitting severe working below the equiaxing temperature. The pure metal may be nearly as soft as copper, but the hardness is increased by heat treatment, dissolved gases, or small amounts of other impurities. Hardened tantalum approaches the agate in hardness and carries a keen cutting edge, but the hardening of the metal may be carried to such a degree that it becomes brittle. The linear coefficient of expansion is slightly less than that for platinum, hence it may be sealed into glass. The electrical resistance is three times that of tungsten and eight times that of copper. When a strip of tantalum is made the cathode in an ordinary electrolyte, the current passes without interruption; but when this metal forms the anode, it is quickly coated with an irridescent blue oxide which seems to offer great resistance to the passage of the current.

When a bar of the metal is heated in the air, the surface turns blue at 400°, and at 600° a grayish black coating appears; while at higher temperatures a layer of the white oxide forms on the surface, while a thin wire will burn slowly at high temperatures. The powdered metal if heated red hot will decompose water. When tantalum wire is heated in hydrogen it absorbs large volumes of the gas, 740 volumes being taken up at dull red heat. If the wire is then heated to full red in a vacuum, about three-fourths of the hydrogen is expelled. The remaining hydrogen seems to form compounds which are metallic in ap-

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[1] Von Pirani and Meyer, *Zeit. Elektrochem.* **17** 908 give 2850°; Waidner and Burgess, *Jour. physique*, **6** 380, give 2900°; recent determinations give a slightly higher value, 2910°.

pearance, stable, brittle, and of high electrical resistance. All the hydrogen is expelled only at the fusion temperature.[1] Tantalum combines readily with carbon, forming carbides which render the metal brittle, and at dull redness it combines directly with nitrogen and chlorine. It resists the attack of all single acids, except hydrofluoric and boiling concentrated sulfuric, which attack it slowly. Aqua regia is without effect at all temperatures, but a mixture of hydrofluoric and nitric acid dissolves the metal readily. Solutions of the alkalies have no effect upon tantalum, but it is attacked by fused alkalies and alkaline nitrates. Molten sulfur is said to have little effect on tantalum, but the vapor of sulfur probably reacts with it. Alloys with iron, tungsten, molybdenum, and other metals are formed.

Uses. — Columbium appears to have no commercial uses at the present time. A patent was granted in the United States in 1916 providing for the use of from 0.1 to 10 per cent of columbium as an alloying metal for tungsten to be used in the preparation of incandescent filaments.

Tantalum, having properties similar to those of columbium but being both more abundant and more pronounced in its desirable properties, seems destined to fill a much wider field of usefulness.

The first successful use of tantalum was as a filament in the incandescent lamp industry. The carbon filament lamp had found no competitor for many years, until in 1898 Welsbach made the first metal filament lamp of osmium. These filaments were very fragile and expensive, consequently they never came into general use. In 1903, the first lamps containing a drawn metal filament were prepared by the use of tantalum wire. These lamps were almost twice as efficient (see Table XXXV, p. 277) as the old carbon filaments and quickly became popular. The first lamps contained a filament with a diameter up to 0.28 mm., but as better methods were developed for drawing the wire the diameter was sometimes less than 0.02 mm. Since tantalum has a lower specific resistance than carbon, the metallic filament must have about 2½ times the length and ½ the diameter as the carbon filament for equal voltage and candle power. The temperature of the filament at full glow is close to

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[1] Piccini, *Zeit. Elektrochem.* 11 555 (1905).

the softening point, so that the double loop familiar in carbon filaments is impossible in the tantalum lamp. To permit the use of a long, thin filament the "spider" support was devised and the filament arranged in zigzag fashion upon it. This has the added advantage of permitting the use of the lamp in any position. It is claimed that 103,000,000 tantalum lamps were sold during the years 1905–11. In later years the tungsten filament has entirely displaced those of tantalum.

Tantalum tools have recently attracted much attention, especially in dentistry and surgery. The metal is hardened by alloying with small amounts of such other elements as aluminium, titanium, tin, boron, silicon, hydrogen, or oxygen. A process resembling case-hardening is sometimes applied.[1] It is claimed that tantalum tools are superior to steel for the reason that they do not rust, that they may be sterilized in acids or in a moderate flame, and that they retain their cutting edge effectively.

As a substitute for platinum, tantalum is usable in many ways because of its resistance to corrosion. The first cost is much less than that of platinum,[2] but the use has not been popular even in times of platinum shortage doubtless because tantalum scrap has little value.

Pens made of tantalum are especially serviceable because of the elasticity, hardness, and resistance to corrosion. The manufacturers of inks have not yet been able to prepare a suitable writing fluid without the use of considerable free acid. As a consequence steel pens corrode quickly. An acid-resisting metal has decided advantages, and when the tantalum tip is hardened in order to reduce the wear, increased efficiency is secured.

Electrodes of tantalum may be used for the removal of silver, copper, zinc, nickel, antimony, or platinum from solution since these metals may be dissolved from the electrodes by acids or aqua regia.[3]

As a material for making standard weights it has the advantage of high specific gravity and resistance to corrosion.

Tantalum will doubtless find application in radio sending and

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[1] See *Brit. Med. Jour.* **32** 724 (1911) and *Dental Rev.* **25** 1210 (1911).

[2] In 1913 tantalum vessels sold for about 55 cents per gram.

[3] Brunck, *Chem. Zeit.* **36**, 1233 (1913); Oesterheld, *Zeit. Elektrochem.* **19** 585 (1913).

receiving tubes. Its usefulness, particularly in sending sets, is increased by the ability of the metal to absorb gases, thus acting as its own "getter" and maintaining a vacuum equilibrium in the bulb.

Perhaps the most promising application of tantalum is as an electrolytic valve in rectifying devices. A very simple arrangement gives excellent results. A strip of lead and one of tantalum form the electrodes, and sulfuric acid of the strength ordinarily used in storage batteries is the electrolyte. When such a system is connected with the usual alternating lighting circuit, the flow of current in one direction is uninterrupted and is almost entirely cut off in the other. Hence, there results a pulsating direct current which is serviceable for charging batteries, electrodeposition of metals and other uses. The efficiency of such a rectifier compares favorably with that of other types and has the advantages of almost unlimited life. The only care required is the occasional addition of a little distilled water to the electrolyte. The voltage of the lighting circuit should be cut down to 18 or 20 by a suitable transformer.

Tantalum alloys readily with many metals, such as iron, molybdenum, and tungsten. Ferrotantalum is made by reduction of a mixture of tantalite and iron ore in an electric furnace. It has been tried in the steel industry.[1] A small per cent of tantalum has a marked effect upon the properties of an alloy and its use as a constituent of alloys may be expected to increase materially. An alloy with nickel containing as much as 30 per cent tantalum has some striking properties.[2] The magnetic quality of nickel is lacking and the alloy may be heated in the air to high temperatures without oxidation. It is not attacked by boiling acids or aqua regia; it is tough and may be rolled or hammered easily. It is made by mixing the two metals in powdered form, compressing at high pressure and heating in a quartz tube in a vacuum. Other alloys of tantalum have been prepared for electric lamp filaments, arc electrodes, spark points, and other uses where resistance to corrosion is desired.[3] An alloy of tantalum containing 60–90 per cent molybdenum is recommended as a substitute for platinum.[4]

[1] Guillet, *Compt. rend.* **145** 327 (1907).
[2] *Mining American*, **76** No. 1939, p. 4 (May 19, 1917).
[3] Brit. Pat. 138,348, Jan. 27, 1920.
[4] U. S. Pat. 1,385,072, July 19, 1921.

Tantalum pentoxide is unchanged at high temperatures and it has been suggested as a refractory.

Compounds of Columbium. — In the majority of its compounds columbium is pentavalent, although it is sometimes trivalent and its oxides present some resemblance to the oxides of nitrogen. There is a marked tendency to form oxy-compounds.

Oxygen forms three oxides of columbium, the dioxide (or monoxide), Cb_2O_2 (or CbO); the tetroxide (or dioxide), Cb_2O_4 (or CbO_2); and the pentoxide, Cb_2O_5. The most important salts of columbium are derivatives of the pentoxide.

Columbium dioxide, Cb_2O_2, is formed by the partial reduction of potassium columbium oxy-fluoride with sodium at a high temperature. It burns in chlorine, forming $CbOCl_3$, liberates hydrogen from HCl, and is so metallic in appearance that Rose mistook it for the element.

Columbium tetroxide, Cb_2O_4, is prepared by heating the pentoxide to a high temperature in an atmosphere of hydrogen or in the presence of magnesium powder. It is a powder which appears black or blue under different conditions, and is not attacked by acids.

Columbium pentoxide, Cb_2O_5, is a white infusible powder obtained by treating the potassium columbium oxy-fluoride with sulfuric acid and extracting with water, or by ignition of columbic acid. It is generally amorphous, but on strong ignition it becomes crystalline. It becomes yellow on heating, is non-volatile, and is not reduced at the temperature of the Bunsen burner. It does not dissolve in acids except hydrofluoric acid, but is dissolved by fused potassium bisulfate.

Columbic acid, $HCbO_3$, is obtained as a white amorphous precipitate when a strong mineral acid is added to a water solution of potassium hexa-columbate. It dissolves somewhat in hot concentrated sulfuric acid, is readily soluble in hydrofluoric acid, but very slightly dissolved by other acids. It dissolves readily in alkaline carbonates and hydroxides; it is slightly more basic than the analogous tantalum compound.

Columbates, analogous to the three classes of phosphates, are recognizable among the minerals: ortho-columbates, $M_3'CbO_4$, pyro-columbates, $M_4'Cb_2O_7$, and meta-columbates, $M'CbO_3$. Of these the meta derivatives are the most important, both in the laboratory and in nature. The mineral columbite is essentially ferrous meta-columbate, $Fe(CbO_3)_2$. Many higher columbates are formed, of which potassium hexa-columbate, $K_8Cb_6O_{19} \cdot 16\,H_2O$, is the most important. It is prepared by fusing the insoluble columbates or Cb_2O_5 with KOH or K_2CO_3.

Percolumbic acid, $HCbO_4$, is prepared by adding H_2O_2 to columbic acid and warming. It is a yellow amorphous powder which differs from other per-acids by the fact that warming is required before it is decomposed by dilute sulfuric acid.

Fluorine forms the pentafluoride, CbF_5, by the action of HF on the pentoxide. It is known only in solution, but forms double salts which are more stable. K_2CbF_7 crystallizes in shining rhombic needles. When salts of the order of $K_2CbOF_5 \cdot H_2O$ are dissolved in hot hydrofluoric acid.

The oxyfluoride, $CbOF_3$, forms as a fine crystalline deposit when Cb_2O_5 is mixed with CaF_2 and heated in a stream of HCl. The oxyfluoride double salts are numerous and important. They are formed when columbic acid is dissolved in HF and varying quantities of alkali fluorides added. Of these $K_2CbOF_5 \cdot H_2O$ is the one obtained in the separation of columbium from tantalum. Marignac obtained many others in crystalline form, such as K_3CbOF_6, $K_5(CbO)_3F_{14} \cdot H_2O$, $K_4(CbO)_3F_{13} \cdot 2H_2O$, etc.

Chlorine forms both a trichloride, $CbCl_3$, and a pentachloride, $CbCl_5$, as well as the oxychloride, $CbOCl_3$.

Columbium trichloride is prepared (1) by passing $CbCl_5$ vapor slowly through a hot tube, or, (2) by heating Cb_2O_5 with PCl_5. It forms a dark, metallic-appearing mass of crystals which are neither volatile nor deliquescent, and they are not decomposed by either water or ammonia. This compound is easily oxidized by HNO_3, and when heated in CO_2 it reacts according to the equation $CbCl_3 + CO_2 = CbOCl_3 + CO$. It is the only metallic chloride which is able to reduce carbon dioxide.

Columbium pentachloride is formed (1) when a mixture of Cb_2O_5 and carbon is heated in air free chlorine, (2) when Cb_2O_5 is heated with S_2Cl_2 or CCl_4 in a sealed tube, or (3) when Cb_2O_5 is heated in an atmosphere of chlorine and carbon monochloride. As generally prepared it is yellow, but the pure product is white or nearly so. It forms needles which sublime at 125° and are soluble in carbon tetrachloride, sulfur monochloride, chloroform, and alcohol.

Columbium oxychloride, called also columbyl chloride, $CbOCl_3$, may be prepared (1) by heating Cb_2O_5 in chlorine, (2) by heating a mixture of Cb_2O_5 with a small amount of carbon in the presence of chlorine, and (3) by repeated distillation of $CbCl_5$ in an atmosphere of CO_2 over Cb_2O_5. It is colorless, crystalline, deliquescent, and vaporized at 400°. Water decomposes it violently, forming columbic acid. It forms double alkali chlorides.

Bromine forms $CbBr_5$ and $CbOBr_3$.

Sulfur forms $CbOS_3$.

Nitrogen unites directly with metallic columbium[1] at 1200°, forming Cb_3N_5.

Compounds of Tantalum **are similar to the corresponding salts of columbium. Tantalum shows a decided preference for the pentavalent state of oxidation, and in its compounds it shows a slightly more basic character than columbium.**

Oxygen forms two oxides, Ta_2O_5 and Ta_2O_4.

Tantalum tetroxide, Ta_2O_4 (sometimes called the dioxide TaO_2), is formed by reducing Ta_2O_5 at very high temperatures with carbon or magnesium. It is a black mass, hard enough to scratch glass, porous, and is

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[1] Moissan, *Compt. rend.* 133 20 (1901); Muthmann, Weiss and Riedelbauch, *Ann.* 355 58 (1907).

not attacked by acids, even a mixture of nitric and hydrofluoric acids being unable to dissolve it. When heated in the presence of air it burns, forming Ta_2O_5.

Tantalum pentoxide is usually prepared in one of two general methods. (1) When a tantalum compound, even the ore, is dissolved in HF and ammonia added, tantalic acid precipitates. This on ignition yields Ta_2O_5. (2) A tantalum compound such as the fluoride is dissolved (or suspended) in strong sulfuric acid and the mixture heated to dense white fumes; on dilution Ta_2O_5 is precipitated. It is a white infusible powder, amorphous when first formed but becoming crystalline when heated to a high temperature. After ignition it is insoluble in all acids, but may be completely vaporized by ignition with NH_4F.

Tantalic acid or tantalum hydroxide is usually given the formula $HTaO_3$, although the composition undoubtedly varies rather widely. It is precipitated as a gelatinous mass when the chloride is diluted, but it may be obtained in crystalline form by precipitation with dilute ammonia. When the crystalline form is ignited it glows brilliantly and forms Ta_2O_5. The freshly prepared acid dissolves quite readily in acids.

Tantalates are numerous, and form important ores of tantalum. Of these the most important is tantalite, which is ferrous meta-tantalate, $Fe(TaO_3)_2$. These salts are all insoluble in water. Both ortho- and pyro-tantalates are known. In addition some important salts are derivatives of the hypothetical hexa-tantalic acid, $H_8Ta_6O_{19}$, whose sodium and potassium salts are soluble in water.

Pertantalic acid, $HTaO_4$, is more stable than percolumbic acid. Its potassium salt is obtained as a crystalline white precipitate when a large excess of hydrogen peroxide is added to a solution of potassium hexatantalate, $K_8Ta_6O_{19}$, and alcohol added. If sulfuric acid is added to the pertantalate, the hydrated acid is liberated.

Fluorine forms tantalum pentafluoride, TaF_5, which resembles the columbium salt, being known only in solution. It forms important double fluorides.

Potassium fluotantalate or tantalofluoride, K_2TaF_7, is formed by dissolving tantalic acid in HF and adding the correct amount of KF. It is sparingly soluble in cold water but dissolves quite readily in hot water. It crystallizes from solution in fine rhombic needles which may be melted without decomposition. When a solution of the fluotantalate is boiled, a white insoluble oxy-fluoride of the composition $4\,KF \cdot 2\,TaF_5 \cdot Ta_2O_5$ is precipitated. Columbium does not behave in a similar manner, consequently this reaction is used to detect small quantities of tantalum in columbium material.

Numerous double fluorides of the types $M'F \cdot TaF_5$, $2\,M'F \cdot TaT_5$, etc., have been prepared.[1]

Chlorine forms two compounds, the pentachloride, $TaCl_5$ and the dichloride, $TaCl_2 \cdot 2\,H_2O$.

Tantalum pentachloride may be formed (1) by heating a mixture of

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[1] See C. W. Balke, *Jour. Am. Chem. Soc.* **27** 1140 (1905).

Ta_2O_5 and carbon in a stream of chlorine, (2) by heating Ta_2O_5 with PCl_5, or (3) by heating Ta_2O_5 in an atmosphere of chlorine and sulfur monochloride. It is white, crystalline, easily volatile, and fumes in moist air, liberating tantalic acid. It absorbs moisture almost as readily as P_2O_5.[1]

Tantalum dichloride, $TaCl_2 \cdot 2H_2O$, is prepared by reduction of the pentachloride with sodium amalgam. It crystallizes from dilute hydrochloric acid in green hexagonal crystals, which are unstable in the air.

Bromine forms $TaBr_5$, which resembles the chloride both in preparation and properties.

Iodine forms no compound with tantalum.

Sulfur forms a tetrasulfide, Ta_2S_4 (or TaS_2), which is prepared (1) by heating Ta_2O_5 to a high temperature in the presence of hydrogen and carbon disulfide, or, (2) by heating $TaCl_5$ in an atmosphere of H_2S. It is insoluble in hydrochloric acid but is oxidized slowly by nitric acid or aqua regia.

Nitrogen forms at least two compounds with tantalum. When the chloride is heated to redness in a stream of ammonia, Ta_3N_5 is formed as a red powder. At a white heat TaN is produced, appearing as a black powder with a distinct metallic appearance.

Detection. *Columbium* may be extracted from any of its ores by fusion with KOH, and extraction of the hexacolumbate with water. The following may be used to identify columbium:

(*a*) If the alkaline solution of hexacolumbate is acidified, columbic acid is precipitated, white, insoluble in HCl, but readily soluble in HF. It is soluble also in hot concentrated H_2SO_4, and is not precipitated on dilution.

(*b*) Ammonia added to the sulfuric acid solution produces a precipitate called "acid ammonium columbate," of uncertain composition. Ammonia produces no precipitate in the presence of tartaric acid.

(*c*) Zinc added to the sulfuric acid solution produces a blue color, which may be concealed by the more intense color produced by tungsten, molybdenum, or vanadium. Titanium also produces a blue which is somewhat less pronounced. For this test HF must be absent.

(*d*) If KF is added to the hydrofluoric acid solution of columbium and the solution evaporated to small bulk, the broad platelike crystals of $K_2CbOF_5 \cdot H_2O$ are deposited.

(*e*) Tannin added to an acid solution containing columbium produces an orange-red precipitate.

(*f*) If to a bead of microcosmic salt a little columbium is added, the color becomes blue in the reducing flame, but changes to violet or brown as the amount of columbium is increased. With the addition of ferrous sulfate, the bead turns red when heated.

Tantalum ores are likewise decomposed by fusion with KOH and the resulting hexatantalate is extracted with water. The following tests may be used to identify tantalum:—

(*a*) If a concentrated solution of potassium hexatantalate is acidified by HCl, a precipitate results, soluble in excess, forming an opalescent liquid.

(*b*) Zinc added to the HCl solution from (*a*) produces no coloration.

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[1] See G. W. Sears, *Jour. Am. Chem. Soc.* **37** 833 (1915) and **39** 1582 (1917).

(*c*) If sulfuric acid is added to the alkaline solution of hexatantalate, tantalic acid is precipitated, white, gelatinous, insoluble in excess; it is dissolved by hot concentrated sulfuric acid and reprecipitated on dilution.

(*d*) Ammonia added to an acid solution precipitates tantalic acid (or acid ammonium tantalate). In the presence of tartaric acid this reaction does not take place.

(*e*) HF dissolves tantalic acid freely, and if the solution is concentrated KF produces a precipitate of K_2TaF_7 as fine needles, which are fusible, slightly volatile, and soluble in 150–160 parts of water. On boiling the solution there appears a fine white precipitate of $K_4Ta_4O_5F_{17}$, very insoluble and quite characteristic.

(*f*) Tannin added to an acid solution produces a precipitate with a yellow color.

Estimation.[1] — Gravimetrically, columbium and tantalum are determined as pentoxide obtained by ignition of the acids. It is customary to determine the amount of the mixed oxides together, then estimate directly the subordinate element and determine the quantity of the predominant element by difference. Gravimetric methods are tedious but are generally regarded as the most accurate.

For the gravimetric determination of columbium, the material is freed from tantalum by the difference in the solubilities of the double fluorides, using the method of fractional crystallization. (See Marignac's method, p. 226.) Finally the material is evaporated with 1 : 1 sulfuric acid until all fluorine is expelled, water is added, and the acid precipitated with ammonia. After ignition and weighing a correction[2] is generally applied for the Ta_2O_5 present.

Tantalum may be determined gravimetrically by a similar method.

Volumetric methods for determining columbium are rapid and fairly satisfactory since tantalum does not interfere. But tungsten, molybdenum, and titanium must be completely removed. The methods depend on the reduction of pentavalent columbium to the trivalent condition by means of zinc, then the oxidation by standard permanganate. Taylor's method[3] makes the reduction in a Jones reductor and the titration in an atmosphere of CO_2. Levy's method[4] carries out the reduction and titration in an atmosphere of hydrogen in a conical flask from which the air is excluded.

A colorimetric method has been proposed by Meimberg[5] for the estimation of columbium. Most of the tantalum is removed as the fluotantalate, then the columbium is reduced with tin in a colorimetric tube. The amount of columbium is determined by comparison with a fresh standard solution. For samples of 10 grams an accuracy of 0.01 per cent is claimed.

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[1] See *Proc. Colo. Sci. Soc.* **11** 185 (1917); for determination of tantalum in alloy steels, see *Compt. rend.* **166** 494 (1918) and *Jour. Ind. and Eng. Chem.* **9** 852 (1917); see also W. P. Headden, *Am. Jour. Sci.* [v] **3** 293 (1922).

[2] See Mellor, *Quantitative Inorganic Analysis*, p. 422; Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*, p. 132; or Johnstone, *Rare Earth Industry*, p. 60.

[3] *Jour. Soc. Chem. Ind.* **28** 818 (1909).

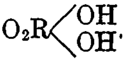
[4] *Analyst*, **40** 204 (1915).

[5] *Zeit. angew. Chem.* **26** 83 (1913).

CHAPTER XIV

GROUP VI — MOLYBDENUM

THE members of Group VI may be divided into two well-defined sub-groups. Of these, the A division, including chromium, molybdenum, tungsten, and uranium, is characteristically metallic in nature; while the B division, consisting of oxygen, sulfur, selenium, and tellurium, is distinctly non-metallic. The metallic elements have high melting points and the metals are produced with difficulty, while the non-metals are gaseous or easily vaporized, with both the melting points and boiling points increasing with increase of atomic weight. Each of the metallic elements of this Group unites with each one of the non-metallic elements, the compounds formed showing close resemblances. All members of the Group (except oxygen) form trioxides which have distinctly acidic properties. These trioxides form well-defined compounds of the type $M_2'RO_4$, in which M' is hydrogen or a univalent metal and R is a member of this Group. In general the series of salts derived by substituting a single metal for M, but varying R, are isomorphous with striking analogies. There are also many compounds formed, in which one equivalent of the basic oxide unites with several equivalents of the acidic oxide, such as dichromates, disulfates, diuranates, and polytungstates.

The normal acids derived from the trioxides have a constitution represented graphically thus:  $O_2R\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$. Not only may the hydrogen of these acids be replaced by metallic elements, but the hydroxyls may be replaced by negative radicals like the halogens. The chlorides so formed, such as SO_2Cl_2 and CrO_2Cl_2, behave like the non-metallic chlorides since they are promptly hydrolyzed by water. But as the atomic weight of the element increases, the stability of the compound becomes greater since the radical RO_2 becomes more basic. Finally in the uranyl compounds we find the radical UO_2 forming the most stable and best known uranium salts.

In the dioxides, the non-metallic members of the Group form compounds which are rather feebly acidic. The dioxides of the metallic elements are basic in nature; other basic oxides, such as RO and R_2O_3, are also formed. These oxides give rise to series of salts which are generally active reducing agents, owing to the tendency to form hexavalent compounds.

The non-metallic elements combine with hydrogen and the alkyl radicals yielding volatile compounds. No such derivatives of the metallic members of this Group are known.

In valence Group VI shows a wide variation. Oxygen is almost always bivalent, though occasionally it is probably quadrivalent. The elements sulfur, selenium, and tellurium are always bivalent toward hydrogen and the alkyl radicals, while in other compounds the valence may be two, four, or six. The metallic elements show a variety of valences, though all members of the Group have a valence of six in their most characteristic oxygen compounds.

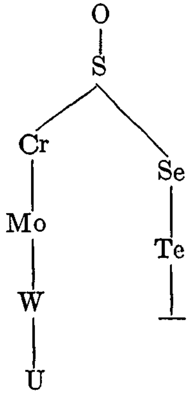


FIG. 14

The relationship between the members of the Group is shown in Fig. 14. The blank space following tellurium is occupied by polonium and its isotopes.

TABLE XXXII

Physical Properties[1] *of the Chromium Sub-Group*

	CHROMIUM	MOLYBDENUM	TUNGSTEN	URANIUM
Atomic Weight	52.0	96.0	184.0	238.2
Specific Gravity	6.74	9.01	19.13	18.7
Atomic Volume	7.7	10.6	9.6	12.7
Melting Point	1550°.	2535°.	3267°.[2]	1500°.[3]

MOLYBDENUM

Historical. — The name molybdenum is derived from words appearing in both Latin and Greek literature, where it was used in reference to any

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[1] See also table by C. W. Balke, *Chem. and Met. Eng.* **27** 1273 (1922).

[2] Langmuir's value.

[3] The melting point of uranium is given by various authorities all the way from 800° to above 1850°.

black mineral which left a mark on paper. The term was applied to such substances as galena, stibnite, plumbago, and graphite. For many years there was no distinction made between graphite and molybdenum sulfide, since their physical properties are so similar. In 1778–79 Scheele showed that by heating molybdenite with nitric acid there was obtained sulfuric acid and a peculiar white earth, which also had acid properties. For the earth he suggested the name acidum molybdenae, and argued that the mineral was molybdenum sulfide. In 1782 Hjelm prepared the metal, and in 1797 Klaproth called attention to the difference between molybdic and tungstic acid, and soon after Berzelius explained the chemistry of many of the compounds of molybdenum.

Occurrence.[1] — The chief ores of molybdenum are molybdenite, MoS_2, containing 60 per cent of the element, wulfenite, $PbMoO_4$, containing 37–40 per cent MoO_3, and molybdic ocher, sometimes called molybdite, $Fe_2O_3 \cdot 3MoO_3 \cdot 7\frac{1}{2}H_2O$, containing 57–59 per cent MoO_3. Recently the mineral powellite, $CaMoO_4$, containing 65 per cent MoO_3, has become commercially important.

In addition molybdenum is found in several more rare minerals which have not been fully studied and are of no importance as sources of molybdenum. It is a frequent constituent of the ores of other metals, especially in iron ores, from which it finds its way into both pig iron and slag. It has been known to accumulate to the extent of 28 per cent in slag from blast furnaces. It also is found in appreciable amounts in the residues from copper smelting ovens, but it is never found in the free state. The lines of molybdenum are recognizable in the solar spectrum.

The principal commercial ore of molybdenum is molybdenite, which occurs usually in flakes which are soft, greasy, easily friable, leaving a bluish gray streak on paper and a slightly greenish streak on porcelain. The hardness ranges between 1 and 1.5 and the specific gravity between 4.7 and 4.8. It resembles graphite closely in physical appearance, but may be distinguished from the latter by the specific gravity,[2] color of the porcelain streak, and the fact that on heating molybdenite in a closed tube the odor of sulfur dioxide is readily obtained.

The development of the molybdenum industry proceeded very slowly for many years. Steel makers were unwilling to experiment with molybdenum as a component of alloy steels

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[1] See *Bull.* 111, Bureau of Mines (1916).

[2] Graphite has a specific gravity of 2.09–2.23 and it leaves a lead-gray streak on both paper and porcelain.

because the mineral was mined in small quantities and a steady supply was quite uncertain. On the other hand those in control of the low grade molybdenum ores were unwilling to begin mining on an extensive scale because of the fact that the demand was small. Consequently mining operations were confined to a few high grade deposits where hand methods were largely used. With the outbreak of the European war there came a sudden and extensive demand for steel hardening metals, which directed attention toward molybdenum. As a means of stimulating production the British Government guaranteed a price at Ottawa of $1.09 per pound of MoS_2 in 85 per cent concentrates. Under the stimulus of high prices and heavy demand, the molybdenum industry grew rapidly in various parts of the world so that production increased at an enormous rate.

The business depression which followed the close of the war was particularly disastrous to the molybdenum industry. The demand for molybdenum products was suddenly cut off, stocks piled up, and mining operations were almost entirely suspended. This natural condition was doubtless exaggerated by the fact that in 1917 Great Britain bought nearly the entire output of the Norwegian mines in order to keep the material from going to Germany.[1] The price paid was as high as $4.25 per pound. After the war this accumulated stock was thrown on the market at greatly reduced prices. During 1919–20 there was almost no production of molybdenum in either the United States or Canada and no importations, in spite of the fact that the low rate of exchange made high grade foreign molybdenum available at a surprisingly low rate.

Molybdenum ores are widely distributed over the earth's surface, workable deposits being found in Norway, Sweden, Finland, Saxony, France, Italy, Belgium, Spain, South Africa, Newfoundland, Canada, Australia, New Zealand, Prince of Wales Island (Alaska), Peru,[2] Japan, and the United States. Deposits are known in New England, New York, Pennsylvania, Colorado, and California. Up to recently practically all the world's supply of molybdenum came from Queensland, New South Wales, and Norway. In 1910 Queensland produced 50 per cent of the world's production, in 1915 the United States

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[1] *Eng. and Min. Jour.*, Jan. 18, 162 (1919).

[2] Otto Wilson, *Chem. and Met. Eng.* **26** 700 (1922).

was the chief producer; in 1917 Canada led the list of producers, and in 1918 the United States marketed the equivalent of 430.8 tons of the metal, the largest amount ever produced by any country. A small amount of the American deposits is mined in California and Arizona, but most of it comes from Colorado, which is said to contain molybdenum deposits in every one of its mining counties, but with only one or two of these developed. One of the most interesting developments in the molybdenum industry has been made at Climax, Colorado, where the ore is estimated as sufficient to supply 1000 tons per day for more than 30 years. This ore is remarkably uniform and contains 11 pounds of molybdenite per ton. The mine is near Leadville at an elevation of 11,000 feet. Great difficulties are encountered because of the deep snow which continues during a large part of the year. The mill and the mine, which are about a mile apart, are connected by a wire rope tramway.

Concentration of such an ore is absolutely essential to the success of the industry. Concentration by rolling and screening has been tried, but it is too wasteful to be successful except in conjunction with other methods of concentration. Electrostatic separation is applicable to certain ores, but the most efficient concentration in most cases is accomplished by flotation. At Climax the concentration is accomplished by flotation in an alkaline solution, the concentration ratio being 1 : 125.

Concentration of wulfenite ores is a much more simple process since efficient concentration is accomplished by almost any of the wet processes, or if water is not available, pneumatic separators are effective. Wilfley tables, working on milled ore containing 2 per cent Mo, are capable of concentrating 85 per cent of the molybdenum even in the presence of so heavy a gangue as barium sulfate.[3]

A high grade molybdenite concentrate will contain 90-95 per cent MoS_2, though much lower grades are sometimes sold. Molybdenite is sold on the basis of the molybdenum content reckoned as MoS_2, but wulfenite may be sold either on the basis of the metallic molybdenum or of the MoO_3. These three methods of calculation are unfortunate and lead to much confusion. The price of molybdenite has shown very great fluctuations. A few years ago MoS_2 could be purchased for

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[3] *Jour. Frank. Inst.* **189** 47 (1920).

15 to 30 cents per pound. In 1908 high grade molybdenite containing 90–95 per cent MoS_2 sold in the European market for 32–38 cents per pound, but the price rose steadily until in 1915 it was $1.20–$1.85 per pound. In 1917 small lots were sold for $2 per pound. Following the war the price dropped rapidly, and in New York in 1919, 90 per cent MoS_2 sold for 65–75 cents per pound; this price prevailed in February, 1923.

Extraction. — The extraction of molybdenum salts from native ores may be accomplished in several ways, some of the methods which are in actual use being secret. Naturally, the method selected will depend upon the kind of ore, the other metals present, and various other considerations. Some of the available methods are outlined as follows: —

I. From molybdenite, the extraction may be made in several ways. (*a*) The mineral is roasted as long as sulfur dioxide is given off. The residue which contains MoO_3 is leached with dilute ammonia and the solution evaporated until the ammonium molybdate crystallizes. Japanese patent 37420 (1920) extracts the roasted ore with Na_2CO_3 solution, then precipitates calcium molybdate by adding $CaCl_2$.[1] (*b*) The finely ground ore is heated with nitric acid and the MoO_3 dissolved in ammonia. (*c*) A current of chlorine is passed over the dry pulverized ore at a temperature of 268°. The molybdenum chloride distills over and may be separated from sulfur and other chlorides by fractional condensation.[2] (*d*) A British patent describes the extraction with an alkaline sulfide or polysulfide solution which removes the molybdenum from the ore as the soluble thiomolybdates. These may be converted to the molybdates by acidification or by contact with more ore.

II. From wulfenite the extraction of molybdenum presents greater difficulties because of the larger number of metals present. This consideration and the facts that wulfenite has a small molybdenum content and is at the same time much more rare than molybdenite, have led to the prediction[3] that wulfenite will not become an important source of molybdenum. On the other hand the wulfenite has the advantage of containing other valuable metals, the recovery of which materially decreases the cost which must be assessed to the molybdenum. Previous to 1915 most of the American material was obtained from wulfenite, but fully 90 per cent of the present supply comes from molybdenite.[4]

The extraction methods applied to wulfenite may in general be grouped as follows: (*a*) acid leach requires a large excess of strong acid in order to bring the material into solution, then much alkali to neutralize the ex-

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[1] See, also, U. S. Pat. 1,403,477, Jan. (1922).

[2] U. S. Pat. 1,398,735.

[3] *Min. and Scientific Press*, **117** 529.

[4] *Chem. and Met. Eng.* **21** 364 (1919).

tract. Special methods are required to separate the lead, and as a consequence this method of extraction is long, complicated, and expensive. (b) In the alkaline leach the ore is treated with sodium sulfide. This leaves the lead, antimony, silver, and gold in the residue in such form that the extraction of these metals is easily accomplished. From the extract the molybdenum may be precipitated as MoS_3, which may be readily transformed to ammonium molybdate or used in making ferromolybdenum, or it may be added directly to molten steel to give the alloy steel, since either carbon or silicon of the steel will reduce the molybdenum to the metallic state. (c) Several fusion methods are recommended. If the ore is fused with potassium polysulfide and the mass extracted with water, the soluble molybdenum sulfo-salts are separated from the insoluble lead sulfide. If the ore is mixed with an excess of sodium carbonate containing carbon and charged into a lead blast furnace, lead, silver, and gold are recovered as bullion and sodium molybdate appears in the slag. The latter may be leached out with water, or if the slag is rich enough in molybdenum, it may be used in an electric furnace to produce ferromolybdenum. Fusing with sodium carbonate, sodium hydroxide, and carbon is efficient in that it removes 95 per cent of the lead and molybdenum at a relatively low cost. Any fusion method, however, may produce trouble because the strongly alkaline slag attacks the furnace lining.

Molybdenum comes into the market in various forms, depending on the use to be made of it. Ammonium molybdate goes chiefly to the chemical laboratories. The industries use some ammonium molybdate though the oxide is the usual form required. The metal is sold in powder form, as rods or wire, and very largely as the iron alloy.

Separation. Molybdenum belongs to that group of elements whose sulfides, precipitated by H_2S from acid solution, are soluble in alkaline sulfide solutions. Molybdenum sulfide, however, is difficult to precipitate from acid solutions, consequently it is necessary to carry out the reaction in a pressure bottle. This method furnishes a satisfactory separation of molybdenum from chromium, vanadium, and the other members of the third group.

An approximate separating of molybdenum and tungsten from other metals may be carried out as follows. Group II metals may be precipitated with hydrogen sulfide without the use of the pressure bottle. The filtrate is made alkaline without boiling and more H_2S added. This precipitates the third group, but molybdenum and tungsten remain in solution as the soluble sulfo-salts. After filtering off the third group precipitate, the filtrate is acidified when both tungsten and molybdenum sulfide are thrown down. This method works well in qualitative analysis.

Iron may be removed by the hydrogen sulfide pressure bottle precipitation, but a much more convenient method is to oxidize the iron to the ferric condition, then pour the solution into a hot 10 per cent solution of sodium hydroxide. Boil for a time, cool, filter, and wash the ferric hydroxide thoroughly. If much iron is present the precipitate should be dissolved in acid and the precipitation repeated. Iron may be successfully removed by two or more precipitations with ammonia.

Arsenic (or phosphorus) may be removed by adding ammonia to the solution containing arsenic (or phosphoric) acid, then adding magnesium chloride mixture slowly and allowing the precipitated magnesium ammonium arsenate (or phosphate) to settle overnight. For a complete separation the precipitate should be dissolved in acid and the process repeated one or more times. Arsenic has also been removed from molybdenum by distilling off the volatile chloride with strong hydrochloric acid in the presence of reducing agents.

Antimony may be separated from molybdenum by boiling the solution of their chlorides, containing an excess of HCl but no nitrates or sulfates, with sheet lead. Metallic antimony is precipitated while molybdenum is reduced but remains in solution.

Tin is left in solution if molybdenum sulfide is precipitated in the presence of oxalic acid by hydrogen sulfide in a pressure bottle. In ores if cassiterite is present, it may be left with the insoluble residue by dissolving the molybdenum with an acid.

Tungsten may be separated (1) by precipitating molybdenum sulfide under pressure in the presence of tartaric and sulfuric acids; (2) by evaporating a solution of sodium molybdate and tungstate to dryness, heating with an excess of sulfuric acid, then adding a few drops of nitric acid to reoxidize the lower oxides, and dissolving the molybdenum in water. The tungstic acid is not dissolved; (3) by dissolving MoO_3 from a mixture of the trioxide by sulfuric acid of specific gravity 1.37;[1] (4) by passing HCl over the oxides at 250°–270°, the volatile $MoO_3 \cdot 2\,HCl$ is distilled away;[2] (5) by precipitating tungsten acid with

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[1] *Jour. Am. Chem. Soc.* **22** 1772 (1900).

[2] *Compt. rend.* **114** 173 (1892).

stannous chloride;[1] (6) by dissolving MoO_3 from a mixture of the oxides by the use of selenium oxychloride, in which WO_3 is insoluble.[2]

Metallurgy. — Metallic molybdenum may be prepared in several ways: —

(1) By decomposing molybdenite in an electric furnace. The product contains from five to seven per cent carbon, of which about one per cent is in graphitic form.

(2) If a mixture of molybdenite and the dioxide is heated in the electric furnace, the reaction takes place readily: $MoS_2 + 2MoO_2 = 3Mo + 2SO_2$. This process is capable of producing 98.5 per cent molybdenum with only 0.7 per cent of sulfur.

(3) By the reaction of hydrogen on the hot oxide, chloride, or ammonium salt.

(4) By reduction of the oxide by the Goldschmidt process. This produces a metal 98–99 per cent pure, containing small percentages of iron and silicon as impurities, but quite free from carbon.

(5) Reduction of the oxide with carbon is successful, but the product always contains carbon, the per cent of which increases if the charge is heated too much. If carbon bearing molybdenum is melted with the oxide of the metal, the pure metal may be obtained. A purity of 99.98 per cent is reported, a trace of slag being retained. Sometimes lime is mixed with the charge, the reaction being $MoS_2 + 2C + 2CaO = Mo + 2CaS + 2CO$. The metal prepared by this reaction may contain as much as 3 or 4 per cent of sulfur.[3]

(6) The oxide may be reduced with misch metal.

(7) If MoO_3 is made into a paste with dilute H_2SO_4 and electrolyzed, a lower oxide is obtained from which the metal is obtained by reduction in hydrogen.

Properties. — Molybdenum is usually obtained as a gray metallic powder which may be sintered into the compact form by pressing into bars and heating by the electric current in an atmosphere of hydrogen. In the coherent form it is usually a little darker than platinum though the pure metal is said to be silvery white. The pure metal is tough and malleable, but im-

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[1] E. E. Marbaker, *Jour. Am. Chem. Soc.* **37** 86 (1915).

[2] H. B. Merrill, *Jour. Am. Chem. Soc.* **43** 2383 (1921).

[3] Brit. Pat. 181,837 (1921) and Can. Pat. 221,041 (1922).

purities make it brittle and even fragile. It is not hard enough to scratch glass, and it may be filed and polished easily and it may be forged while hot. Formerly molybdenum was said to be totally lacking in the property of ductility, but recently a method has been devised for producing a ductile form from which fine wire may be drawn. The melting point has not been accurately determined, but it is placed around 2500° C., having the highest melting point of all metals except osmium, tantalum, and tungsten. The specific gravity increases appreciably as the metal is subjected to mechanical working. Moissan obtained a value of 9.01, but the ductile metal after drawing has a specific gravity as high as 10.32. The Brinell hardness is 147. The tensile strength increases materially with the fineness of the wire, as is shown in Table XXXIII.

Table XXXIII

Tensile Strength of Molybdenum, Tungsten, and Steel

In kilograms per square mm.

Diameter in mm.	Molybdenum	Tungsten	Steel
0.125	140–182	322–343	—
.070	161–189	336–371	—
.038	189–217	385–420	—
.075	—	—	356

The electrical resistance of ductile molybdenum at 25° is 5.6 microhms per cubic centimeter for hard drawn wire and 4.8 microhms for annealed wire. The temperature coefficient of electrical resistance between 0° and 170° C. is 0.005. The specific heat is 0.072.

If pure molybdenum is packed in carbon and heated to 1500° C., it absorbs carbon and takes on quite different properties. After absorbing carbon the color becomes gray, it is brittle and hard enough to scratch steel and quartz, and both the melting point and the specific gravity are lowered.

At ordinary temperatures the compact form of molybdenum is slowly oxidized in the air, but the ductile form seems to retain its luster almost indefinitely. On heating to a dull red, a coating of the white trioxide forms slowly and at 600° it burns rapidly. Molybdenum [illegible] ordinary temperatures, with chlorine [illegible] bright red, but with iodine there [illegible]. It is not attacked by [illegible] acid, but hot concentrated [illegible] nitric acid dissolves it rapidly. It [illegible] alkalies, but it is rapidly attacked [illegible] such as $KClO_3$, KNO_3, and Na_2O_2. [illegible] directly with sulfur, nitrogen, phosphorus [illegible]

Uses. Molybdenum [illegible] applications both as a metal and as [illegible]. These uses are being rapidly extended [illegible] considerable amount of research which is being [illegible] interesting element.

In artificial lighting devices molybdenum has been used in a variety of forms. [illegible] use is as a support for the tungsten filament. In the high candle power nitrogen or argon filled lamps the supports need to be relatively large and strong, so considerable [illegible] is used in such lamps. An alloy consisting of 20 per cent molybdenum and 80 per cent tungsten[1] makes an efficient [illegible] filament. Ferromolybdenum has been used also as an electrode in arc lamps.[2] In both the arc and [illegible] molybdenum is an efficient means of [illegible] brilliant light.

Molybdenum wire is very effective as a winding for electric resistance furnaces, because it is cheaper than platinum and is capable of producing a higher temperature. It has the disadvantage of requiring protection from the air to prevent oxidation, though there is a decided advantage from the fact that molybdenum resists the alloying influence of many liquid metals even at high temperatures.[3]

In devices for making and breaking the electric circuit molybdenum serves well on account of the high conductivity of the ductile form. Its relative low cost gives it a decided advantage over platinum and platinum-iridium. It has the disadvantage of forming a non-conducting oxide but this is effectually prevented by use of larger sized devices, in which case there is formed a thin coating of oxide which does not interfere. Duc-

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[1] U. S. Pat. 1,308,907. [2] *Min. and Scientific Press* 104 [illegible] (1912).
[3] *Trans. Am. Electrochem. Soc.* 17 [illegible]

tile molybdenum is also used in the manufacture of certain X-ray tubes and voltage rectifiers.

Molybdenum has been used with tungsten as a thermocouple for high temperature measurements.[1] Such a combination can be used at a much higher temperature than any of the commonly used thermocouples of platinum group metals. Their use is complicated by the fact that to prevent oxidation the metals must be protected with some resistant substance like fused magnesia.

Molybdenum has shown its usefulness in dentistry and in the manufacture of standard weights. The metal also finds extensive use in making audion tubes for amateur wireless outfits, where it replaces platinum in the grid, and in higher powered tubes, where it forms the plates.

In *non-ferrous alloys* molybdenum gives some interesting results. If MoO_3 and WO_3 are mixed together in any proportion and the mixture heated by an electric current in an atmosphere of hydrogen, alloys are obtained which may vary from pure tungsten to pure molybdenum. These alloys are not only useful in making incandescent filaments, but have been suggested as substitutes for platinum. Two difficulties are encountered in their uses: they oxidize readily and cannot be soldered easily. Both obstacles are overcome if the alloy is coated with a layer of a noble metal.

A series of alloys of the "stellite"[2] type include varying proportions of molybdenum, chromium, and cobalt with small amounts of iron, manganese, etc. The addition of molybdenum to an alloy of cobalt and chromium increases the hardness in proportion to the amount of molybdenum added, up to 40 per cent, when the alloy is exceedingly hard and brittle. The usual alloy of this type contains 20–25 per cent molybdenum; it is hard enough to scratch glass, takes a keen edge, and retains its bright color in the air.

An alloy of cobalt and molybdenum has the same coefficient of expansion as glass, and can readily be drawn into wire. Patents have been issued[3] for acid resisting alloys containing about

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[1] L. E. F. Northrup, *Chem. and Met. Eng.* **11** 45 (1913).

[2] See discussion of stellite under tungsten and especially the article by the inventor, Elwood Haynes, *Trans. Am. Inst. Min. Eng.* **44** 576 (1912); *Trans. Am. Electrochem. Soc.*, Apr., 1920, p. 377.

[3] U. S. Pats. 1,375,082 and 1,375,083, Apr. 19, 1921.

10 per cent molybdenum with cobalt or nickel and a little iron or manganese.

Ferromolybdenum is an alloy which is destined to become of great importance, if molybdenum steels are able to compete successfully with other alloy steels. The manufacture of ferromolybdenum is usually carried out in an electric furnace, the charge being a concentrated molybdenite with some iron ore and a suitable flux.[1] As usually carried out the production of ferromolybdenum is a wasteful process, the loss sometimes running as high as 20 or even 30 per cent of the molybdenite. A recently projected plant at Flekkefjord, Norway, has the advantages of the cheap electrical energy, abundant ore, and a nearby market. The process used is claimed to be much more economical than those usually employed.[2] One of the great difficulties which has hindered the development of molybdenum steel has arisen from the impossibility of obtaining a ferromolybdenum of uniform purity. The varying percentages of carbon, sulfur, and other impurities cause great variation in the qualities of molybdenum steel.

Molybdenum steels are not new, since they were manufactured in the United States on a commercial scale as much as a quarter of a century ago.[3] But there is no point in the whole steel industry about which there is so much conflicting testimony as is to be found about the merits of alloy steels containing molybdenum. There are many reasons for this state of affairs, as is shown by a study of the history of this element in steel making. The first results were obtained with ferromolybdenum which contained so much sulfur, oxides, and other injurious ingredients that the products were almost worthless. Later when a purer form of ferromolybdenum was used, improper heat treatment failed to bring out the desirable qualities of the steel and even developed highly objectionable properties. It is no wonder that these early experiences have given molybdenum a bad reputation which has not yet been overcome. On the other hand the friends of molybdenum have claimed superior properties for this alloy steel and have been active

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[1] See "Ferromolybdenum in Canada," *Can. Chem. Jour.* **2** 208 (1918); also U. S. Bureau of Mines, *Bull.* 77 (1916), pp. 146, 151.

[2] *Eng. and Min. Jour.*, Jan. 18, 1919, p. 162.

[3] *Chem. and Met.* **24** 305 (1921).

in a campaign to bring it into popular favor. Whatever the real merits of molybdenum steel may be, it is impossible at the present time to predict its future. It is to be hoped, however, that as information is gained upon the methods of manufacturing and the properties of this alloy steel it will find a place of its own among the useful steel products.

Molybdenum is sometimes the principal alloying element in the steel, but generally it is used with other substances, especially chromium, nickel, tungsten, or vanadium. In general the effect of molybdenum is similar to tungsten, but a small per cent of molybdenum produces the same effect as a much larger proportion of tungsten. Using slightly different methods of comparison, various investigators have estimated the effective ratio of molybdenum to tungsten as between 1 : 2 and 1 : 3;[1] 1.225;[2] and even 1 : 4.[3]

Molybdenum steel is made by the crucible process, by the electric process, by the open hearth, or even directly by heating a mixture of the ores with coke and a suitable flux in an electric furnace.[4] The molybdenum may be added as the powdered metal, but ferromolybdenum[5] is more commonly used because its melting point is lower and it is less liable to suffer from oxidation. When chromium, nickel, and other alloying metals are desired these are at times added as the molybdenum alloy. On account of the difficulties encountered in adding either molybdenum or its ferro alloy it has been suggested that the addition may well be made as calcium molybdate. This practice has proven successful, although special precautions are necessary to prevent loss of material through dusting. The addition is generally made long enough before the metal is drawn to insure a uniform mix. The per cent of molybdenum added is very frequently less than 1 per cent, though 1.5–2 per cent molybdenum is common in high speed steels, and in certain acid resisting steel the amount of molybdenum may run as high as 5 per cent. Steels containing 6–10 per cent molybdenum have been made.

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[1] Swinden, *Carnegie Scholarship Memoirs, Iron and Steel Inst.*, London, **3** 66 (1911); **5** 100 (1913).

[2] W. Giesen, *ibid.* **1** 34 (1909).

[3] L. Guillet, *Revue de Metallurgie*, 1904, p. 390.

[4] R. M. Keeney, *Carnegie Scholarship Memoirs, Iron and Steel Inst.*, London, **4** 173 (1912).

[5] See *Zeit. Metallkunde*, **12** 238 (1920).

The properties claimed for molybdenum steel[1] are increased hardness, toughness, elasticity, and tensile strength. The hardness produced by molybdenum is spoken of as deep hardness, in contrast to the effect of case hardening. In large sections which have been quenched it is usual to find considerable variation in the hardness between the center and the edges. This variation in hardness is less marked in the case of molybdenum steel than it is in other alloy steel. Experiences are on record which seem to indicate that the degree of hardness increases with age until it is scarcely scratched by a drill. For that reason this variety of steel is especially adapted for the manufacture of safes and bank vaults. The claim is made that molybdenum steels machine better than other steels of equal Brinell hardness. Hence any part which must be machined after heat treatment may be harder if formed of molybdenum steel.

It is claimed that the addition of molybdenum to steels of the chrome-nickel type produces higher tensile properties, elastic ratio, and reduction of area, hence increased toughness.[2] Thus by test the addition of less than 0.5 per cent molybdenum with lower nickel and slightly lower chromium content increased the elastic limit from 116,700 pounds per square inch to 130,000; the ultimate tensile strength from 135,200 pounds per square inch to 142,000 pounds; elongation from 19.5 per cent to 20.5 per cent; and the reduction of area 57.1 per cent to 65.0 per cent.

Heat treatment is of great importance in the case of alloy steels, but molybdenum steels have an extremely wide range for practical heat treatment. Thus a steel containing 0.2 per cent carbon and 0.7 per cent molybdenum when quenched in oil from temperatures varying from 870° C. to 1100° C. and drawn at 540° C. showed only slight variations in elasticity and strength.[3] It is also claimed that molybdenum steel permits

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[1] Compare G. W. Sargent, *Trans. Am. Soc. for Steel Treating*, 1 580 (July, 1921); M. H. Schmid, *ibid.* 1 500 (June, 1921); Charles McKnight, *ibid.* 1 288 (Mar. 1921); *Chem. and Met.* 24 395, 927 (1921); A. H. Hunter, *Blast Furnace and Steel Plant*, 9 326, 429 (1921); G. N. Sargent, *Iron Age*, 108 579; *Engineering*, 112 350 (1921); H. J. French, *Trans. Am. Soc. Steel Treating*, 2 769 (1922); C. N. Dawe, *Iron Age*, 109 725 (1922).

[2] Charles McKnight, *Trans. Am. Soc. Steel Treating* 1 288 (March, 1921); also Arthur H. Hunter, *Chem. and Met.* 25 21 (1921); H. J. French, *ibid.* 25 713 (1921).

[3] Charles McKnight, *loc. cit.*

a higher drawing temperature in order to obtain the same physical results; also that as regards forgeability the working range is wider, while it flows better under the dies. One difficulty experienced in the heat treatment of this alloy steel arises from the relative volatility of the molybdenum, leaving the surface without the beneficial effect of the molybdenum. This may be overcome by grinding off the surface layers.

The undesirable properties said to be produced by molybdenum are red-shortness, and the appearance of cracks while rolling or forging. This results in a lack of dependability which is not permissible. In molybdenum tool steel, some users report that cracks are produced by the quenching process; others that they do not hold a thin cutting edge after retreatment as well as before; some find that such tools show irregular cutting speeds, that the material is seamy, and contains physical imperfections.

These imperfections are probably due in the main to the use of impure materials in the manufacture of the steel or to improper heat treatment or subsequent handling. It is claimed that these difficulties can be overcome by more intelligent practice and by properly selected adjunct hardening elements. There seems to be a general impression among steel makers that molybdenum is to be regarded as a more or less unsatisfactory substitute for tungsten or at best as a secondary component of alloy steels whose presence permits a material economy in the quantity of tungsten needed for any desired effect.

The cost of molybdenum is in normal times around $2.50 per pound. This seems like a prohibitive factor in itself, but considering the small amount required to produce any desired result, the small per cent of rejections, the long life and efficient performance, the friends of this alloy steel claim that it can compete successfully with other steels in final cost.

The uses of molybdenum steel are varied. Straight molybdenum steels are not extensively used because the beneficial results of molybdenum are best realized in the presence of some other alloying metal. Chrome-molybdenum steels, commonly containing 0.25–0.40 per cent molybdenum, are becoming widely used in the manufacture of automobiles, tractors, and general machinery. It is particularly serviceable for gears, shafts, and connecting rods. A steel containing more carbon and up to one per cent molybdenum has been successfully used in making springs since the high drawing temperature reduces the danger of breakage without interfering with the resiliency.

Nickel-molybdenum steel was used successfully in making a light armor for baby tanks though these did not receive actual service tests during the war. Some German large gun tubes were made of nickel-molybdenum steel and showed resistance to erosion.[1]

A nickel-chrome-molybdenum steel was used in the crank shafts of Liberty motors, and the results were highly satisfactory. A chrome-vanadium-molybdenum steel has also been very successful.

Molybdenum has been used successfully as a secondary constituent of high speed tool steels, to which it is thought to impart a finer texture and to insure greater freedom from injury previous to hardening. Very successful results have been obtained with a tool steel containing 0.6 per cent carbon, 4–4.5 per cent chromium, 1–2 per cent molybdenum, and 16–18 per cent tungsten. A steel of similar composition containing 4.25 per cent cobalt and 0.67 per cent vanadium, is stated to do 60 per cent more work than the best straight tungsten steel.[2]

Permanent magnets made from molybdenum steel are particularly successful. This steel usually contains 0.5–0.7 per cent carbon, about 0.5 per cent chromium, and 2–3 per cent molybdenum, though the latter element may run as high as 6 per cent. It retains its magnetism longer than hardened carbon steel and is considered one of the best materials for making permanent magnets.

Certain types of molybdenum steels are also used for the manufacture of projectiles, breech blocks for heavy ordnance, and for boiler plates, especially in torpedo boats.

The popularity of molybdenum steels has been greater in England than in the United States, in part at least because of the greater use made here of tungsten steel. With the partial development of the molybdenum deposits in the west and the assurance that the United States contains ⅘ of the world's visible supply this element has attracted much attention among

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[1] Compare "Molybdenum Steel and Gun Erosion," *J. Coll. Eng.*, Tokyo, Imp. Univ. 9 153 (1918); see C. A. 13 851.

[2] F. L. Hess, "Cobalt," *Mineral Res. U. S. for 1918*, p. 967.

steel makers. During the 18 months preceding August, 1919, about 50,000 tons of molybdenum steel[1] were made in this country.

Compounds of molybdenum find a variety of applications such as its use as a pigment for porcelain or china, in dyeing silk and wool, in coloring leather[2] and rubber,[3] in fire proofing, in disinfectants, and in the synthetic production of ammonia. Compounds of molybdenum are used to preserve cordite which is to be stored in a hot climate.[4] Molybdic acid is used in the preparation of Froehde's reagent, in the manufacture of dyes, and as a reagent for hydrogen peroxide. Phosphomolybdic acid is used as a reagent for alkaloids (Sonnenschein's Reagent) and in testing for alkaline metals. Some salts of molybdenum are used in the production of blue prints because of their ability to react with certain organic compounds in the presence of light. Some molybdenum uranium compounds are both sensitive to light and are themselves radioactive. Molybdenum sulfide cells are sensitive to photoelectric influences, especially at low temperatures; such cells differ from the selenium cells in that they are sensitive to infra red light.[5] Ammonium molybdate is widely used for the detection and estimation of phosphates and for the determination of lead. The Parker rust proofing process consists in cleansing iron or steel by sand blast, then dipping first in sodium carbonate and then in a solution of the acid metaphosphate of molybdenum or tungsten, and finally coating the metal with a special oil.

The carbide of molybdenum is very hard, and by heating in an iron or carbon mold until it becomes crystalline it may be used in making tools, dies, and bearings. Patents have been issued in Great Britain for the preparing of very hard tools by shaping molybdenum, then hardening by adding carbon by means of the cementation process.

Compounds. — In its compounds molybdenum displays valences of two, three, four, five, and six. Of these the first four classes are unimportant and relatively unstable, while most of the compounds met are derivatives of MoO_3. Table XXXIV

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[1] *Chem. and Met.* **21** 153 (1919).

[2] F. Pozzi-Escot, *Compt. rend.* **135** 801 (1902).

[3] F. L. Hess, *Min. Resources U. S. for 1908*, p. 746.

[4] *Min. and Sci. Press*, **108** 860 (1914).

[5] U. S. Bur. of Standards, *Sci. Paper* No. 338.

TABLE XXXIV — *Compounds of Molybdenum*

VALENCE	OXIDE	HYDROXIDE	NATURE	TYPICAL SALTS	CHARACTERISTIC COLOR	CLASS NAME	REMARKS
Mo^{II}	MoO	————	Basic	Mo_3X_6; $Mo_3X_6 \cdot H_2O$	yellow-brown	dihalide	MoX_2 unknown[1]
Mo^{III}	Mo_2O_3	$Mo(OH)_3$	Basic	MoX_3; $MoX_3 \cdot KX \cdot H_2O$	red-violet	trihalide	crystalline; soluble
Mo^{IV}	MoO_2	$Mo(OH)_4$ or $MoO(OH)_2$	Basic	MoX_4; MoS_2	brown-gray	tetrahalide, disulfide	crystalline; decomposition by heat; oxidized in air
Mo^{V}	Mo_2O_5	$Mo(OH)_5$ or $MoO(OH)_3$	Basic	MoX_5; $MoOCl$ Mo_2S_5; $Mo_2O_3(SO_4)_2$	green to black	pentahalide	crystalline; soluble; forms double and basic salts
Mo^{VI}	MoO_3	$MoO_3 \cdot 2\,H_2O$ $MoO_3 \cdot H_2O$	Basic	MoX_6; $MoOX_4$ MoO_2X_2	white-yellow	hexahalide	crystalline
			Acidic	$R_2MoO_4 \cdot H_2O$		normal molybdates	alkali salts soluble
				$R_2Mo_2O_7 \cdot H_2O$		dimolybdates	
				$3\,R_2O \cdot 7\,MoO_3 \cdot H_2O$ or $5\,R_2O \cdot 12\,MoO_3 \cdot H_2O$		paramolybdates	
				$R_2O \cdot 4\,MoO_3 \cdot H_2O$ or $R_2O \cdot 8\,MoO_3 \cdot H_2O$		metamolybdates	
				$XR_2O \cdot YMoO_3 \cdot H_2O$		polymolybdates	

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[1] Double chlorides of bivalent molybdenum, such as $HMo_3Cl_7 \cdot 4\,H_2O$, have been prepared. See Lindner, *Ber.* **55 B** 1458 (1922).

shows the relationship between these classes of compounds. The compounds of lower valence are produced by the reduction of those of higher valence. When a soluble molybdate is reduced by nascent hydrogen a characteristic series of colors is produced as the successive stages of reduction are reached. Oxidizing agents on the other hand readily yield the higher compounds.

Molybdenum shows particular fondness for producing complex salts some of which have enormous molecular weights. For example, there are polymolybdates containing as many as 10 molecules of MoO_3 in combination with one equivalent of the basic oxide, as well as polymolybdates containing larger percentages of the basic oxides. Much confusion exists as to the relationship between these classes of compounds. Forsen contends[1] that all known molybdates can be derived from two acids which he calls molybdic acid, $H_6Mo_3O_{12}$, and metamolybdic acid, $H_6Mo_{12}O_{39}$. Posternak[2] in discussing the so-called paramolybdates claims that they do not form a distinct group, but that they resemble the ortho- or metamolybdates, the differences being due to the degree of hydration. He also expresses the opinion[3] that the usual classification into ortho-, meta-, and para-salts has no basis in fact, but that there are only two groups, which he designates as the hexabasic and tetrabasic polymolybdates. He describes[4] certain very complicated hexabasic polymolybdates of which hexammonium dodecamolybdate, $(HN_4O)_3MoO(O \cdot MoO_2)_{10}O \cdot MoO\,(ONH_4)_3 \cdot 6\,H_2O$, may be taken as an example. In addition to these compounds, molybdenum forms numerous phosphomolybdates which contain P_2O_5 and MoO_3 in the proportions 1 : 5, 1 : 15, 1 : 16, 1 : 18, 1 : 20, 1 : 22, and 1 : 24. There are also arsenomolybdates containing As_2O_5 and MoO_3 in the proportions 1 : 2, 1 : 6, 1 : 16, 1 : 18, and 1 : 20. Other complex salts are formed with the acidic oxides of antimony, vanadium, sulfur, tin, silicon, manganese, and iodine, but these salts are little known.

Oxygen forms definite compounds with molybdenum of the formulæ Mo_2O_3, MoO_2, and MoO_3. There are also reported by various authors many other oxides which are more or less uncertain, such as MoO, Mo_5O_7, Mo_2O_5, Mo_5O_{12}, and Mo_3O_8, Mo_7O_{20}. These complex oxides are usually regarded

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[1] L. Forsen, *Compt. rend.* **172** 215 (1921).

[2] S. Posternak, *Compt. rend.* **171** 1058 (1920).

[3] *Ibid.* **172** 114 (1921).

[4] *Ibid.* **171** 1213 (1920).

as combinations of other oxides, especially MoO_2 and MoO_3 in the form of molybdenum molybdates. See the discussion of the blue oxide of molybdenum below.

Molybdenum monoxide, MoO, is not known except possibly in the hydrated form, $MoO \cdot x\ H_2O$, which is prepared[1] as a black amorphous precipitate by warming a solution of Mo_3Cl_6 in NaOH or KOH. But this precipitate is now more commonly regarded as $Mo(OH)_2$ formed by hydrolysis.[2] The black precipitate turns blue, due to oxidation by the air.

Molybdenum sesquioxide, Mo_2O_3, is prepared by reducing the higher oxides by sodium amalgam or zinc, or by heating $Mo(OH)_3$ in a vacuum, although doubt has been expressed[3] concerning the correctness of the formula. It is black, amorphous, insoluble in acids.

Molybdenum trihydroxide, $Mo(OH)_3$, is a brown or black amorphous mass prepared by adding a fixed alkali to a trihalide, by electrolysis of ammonium molybdate solution, or by hydrolysis of the dihalides in the presence of alkali. It oxidizes in the air but dissolves with difficulty in acids.

Molybdenum dioxide, MoO_2, is prepared by gentle oxidation of Mo_2O_3, by heating metallic molybdenum in the air or steam or by reduction of MoO_3[4] or ammonium molybdate. It is brown in color, with sometimes a blue or violet tint, crystalline, and insoluble in KOH or HCl.

Molybdenum tetrahydroxide, $Mo(OH)_4$, is described as a dark red substance which is precipitated from a solution of ammonium molybdenum tetrachloride by the addition of ammonia. Some workers[5] have considered this precipitate an impure pentahydroxide and deny the existence of $Mo(OH)_4$. However, the compound of the formula $MoO(OH)_2$ has been prepared by the reduction of a solution of ammonium paramolybdate. It is a dark green mass which becomes MoO_2 when dried in a vacuum.

Dimolybdenum pentoxide, Mo_2O_5, is a dark violet powder obtained by gently heating $MoO(OH)_3$ in CO_2. It is soluble in both HCl and H_2SO_4, the solubility decreasing with increase of temperature.

The *hydroxide* of pentavalent molybdenum is generally $MoO(OH)_3$, although other hydroxides have been described. When dilute ammonia is added to a dilute solution of Mo^{V} a precipitate forms which on drying over P_2O_5 has the formula $MoO(OH)_3$. It resembles ferric hydroxide in appearance, dissolves in water, and forms colloidal solutions readily.

Molybdenum trioxide,[6] MoO_3, forms by far the most important series of molybdenum compounds. It is somewhat basic in nature, forming hexavalent halides or oxy-salts, but they are not of great importance. The trioxide is distinctly acidic, forming important series of simple and complex molybdates. MoO_3 is found in pure form in nature and may be prepared

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[1] Blomstrand, *Jour. prakt. Chem.* **77** 96 (1859).

[2] Muthmann and Nagel, *Ber.* **31** 2009 (1898).

[3] Muthmann, *Lieb. Ann.* **238** 108 (1887), and Guichard, *Ann. chim. phys.* (7) **23** 498.

[4] Guichard claims MoO_2 is the only oxide obtained by reducing MoO_3 in hydrogen. *Compt. rend.* **129** 722 (1899).

[5] Klason, *Ber.* **34** 153 (1901), and Guichard, *Compt. rend.* **143** 744 (1906).

[6] H. C. Burger, *Zeit. anorg. allgem. Chem.* **121** 240 (1922).

from the sulfide ore by roasting in air, when the trioxide may be removed by sublimation or dissolved out with ammonia. It may also be prepared by heating molybdenum and many of its compounds in air or by treating the metal and its compounds with HNO_3. It may be obtained as a fine white powder which turns yellow when heated or as a light yellow crystalline mass. It sublimes readily in air, forming small colorless rhombic tablets. It is more soluble in cold water than in hot, and its solution turns both litmus and turmeric paper.

Molybdic acid,[1] H_2MoO_4, is obtained as a white crystalline powder when a solution of MoO_3 in nitric acid is evaporated at ordinary temperatures. The hydrated form, $H_2MoO_4 \cdot H_2O (MoO_3 \cdot 2\,H_2O)$, is obtained when ammonium molybdate solution is acidified with nitric acid and the solution allowed to evaporate spontaneously.

Molybdates of the alkali metals are soluble in water and are easily formed by dissolving MoO_3 in alkaline solution. Molybdates of other metals are insoluble, and are formed by precipitation or fusion methods. The normal salts, R_2MoO_4, are not stable, but readily form polymolybdates or condense with other acidic oxides.

The most important molybdates are the ammonium salts. The salt usually known as "ammonium molybdate" is obtained by evaporating a solution of MoO_3 in ammonia. Its composition corresponds to the formula $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$, the paramolybdate, although conductivity measurements indicate that it is a double salt of the formula $(NH_4)_3H_3Mo_3O_{12} \cdot (NH_4)_2H_4Mo_3O_{12}$[2] and other physical measurements lead to the formula $(NH_4)_{10}Mo_{12}O_{41}$.[3]

Intermediate oxides are formed when molybdic acid or a molybdate solution is reduced by such reagents as sulfur dioxide, hydrogen sulfide, stannous chloride, hydrogen iodide, or hydrazine, or by molybdenum, zinc aluminum, iron, lead, or copper. The resulting solution has a characteristic blue color, commonly designated as "molybdenum blue," which furnishes a characteristic test for the salts of this metal. The fact that the same color is produced by adding a cold dilute solution of MoO_2 in hydrochloric acid to a solution of ammonium molybdate has led to the suggestion that the blue compound is a molybdenum molybdate. Various formulas have been suggested for this compound, such as $MoO_2 \cdot 2\,MoO_3$, which might be considered molybdenum molybdate, $Mo(MoO_4)_2$. Other formulas suggested are Mo_2O_5, which is $MoO_2 \cdot MoO_3$; Mo_5O_{14}, which is $MoO_2 \cdot 4\,MoO_3$;[4] Mo_7O_{20}, which is $MoO_2 \cdot 6\,MoO_3$.[5] It seems probable that several compounds of this order exist, and, as suggested by Junius,[6] these are probably derivatives of molybdic acid, which are analogous to phosphomolybdic acid.

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[1] For summary of the acids of molybdenum, see G. F. Hüttig, *Zeit. angew. Chem.* **35** 391 (1922).

[2] Klason, *Ber.* **34** 153 (1901).

[3] Junius, *Zeit. anorg. Chem.* **46** 428 (1905).

[4] Guichard, *Compt. rend.* **129** 722 (1899); Rogers and Mitchell, *Jour. Am. Chem. Soc.* **22** 350, (1900); Junius, *Zeit. anorg. Chem.* **46** 426 (1905).

[5] Junius, *ibid.* **46** 428 (1905).

[6] *Loc. cit.*

Ammonium phosphomolybdate is obtained by adding to a solution of a molybdate, first ammonia, then a small amount of a solution of orthophosphoric acid in nitric acid. It is thrown down as a canary yellow powder, very sparingly soluble in water and dilute acids. An excess of phosphoric acid prevents the precipitation, while the presence of hydrochloric acid or its salts and of many organic acids (except acetic) hinders the reaction. The precipitate when dried above 130° has a uniform composition represented by the formula $(NH_4)_3PO_4 \cdot 12MoO_3$, in which the ratio $P_2O_5 : MoO_3$ is 1 : 24. The hydrated precipitate undoubtedly has a more complex formula.

Phosphomolybdic acid, $H_3PO_4 \cdot 12MoO_3$, is prepared by treating the ammonium salt with successive small quantities of aqua regia. When the combined extracts are evaporated, lustrous needles crystallize out; these are readily soluble in water and are used as a reagent for alkaloids and to precipitate ammonium, potassium, rubidium, caesium, and thallium. Precipitation takes place in a strongly acid solution, when salts of sodium, lithium, and the heavy metals are not thrown down.

Permolybdic or ozomolybdic acid, $H_2MoO_5 \cdot x\,H_2O$, is obtained as a reddish orange precipitate when MoO_3 is treated with H_2O_2 on a steam bath and evaporated under reduced pressure. Permolybdates of the general formula $M^I_2O \cdot 2\,MoO_3 \cdot MoO_4 \cdot 3\,H_2O$ are obtained when the alkali molybdates are dissolved in H_2O_2. These compounds are not stable but readily yield oxygen on heating.

Detection.[1] Molybdenum is precipitated slowly by H_2S from acid solutions, best at temperatures between 70° and 90°, but complete precipitation cannot be secured without the use of a pressure bottle. MoS_3 dissolves readily in warm $(NH_4)_2S_x$, forming $(NH_4)_2MoS_4$, which on acidification yields the trisulfide. Probably the most characteristic test for the molybdates is the play of colors through blue, green, and dark brown as they are reduced in acid solution by zinc. The trioxide imparts a yellowish green color to the blowpipe flame, and in a borax or microcosmic bead produces a characteristic green color in the reducing flame. When a few drops of sodium phosphate are added to a solution of ammonium molybdate in nitric acid, a yellow color is produced and on warming a heavy yellow precipitate of ammonium phosphomolybdate is formed. A solution of ammonium molybdate gives no color when KCNS is added; but if this mixture is reduced by zinc an intense red color appears which disappears in the presence of hydrogen peroxide but not of phosphoric acid. The color of $Mo(CNS)_4$ is similar to that of $Fe(CNS)_3$, but the appearance of the latter should be prevented by the nascent hydrogen and the presence of H_3PO_4.

The xanthic acid test,[2] said to be able to detect 5×10^{-8} grams of molybdenum, is quite satisfactory. The reagent is prepared by saturating a solution of KOH in absolute alcohol with CS_2, then adding 30% alcohol until a cloudiness appears. This alkaline solution keeps well, but the acid

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[1] See Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*, pp. 165–6; Bureau of Mines, *Technical Paper* 230, p. 4 (1920); Bureau of Mines, *Bull.* 111, p. 8 (1916).

[2] See *Zeit. anorg. Chem.* **108** 73 (1919); also *Chem. Ztg.* **43** 777 (1919).

does not. To test for molybdenum evaporate the solution to be tested to small bulk and add xanthic acid slowly. A red ring forming at the junction of the two liquids indicates molybdenum. Chromates interfere, but chromium in other forms as well as vanadium, tungsten, titanium, and uranium do not. A colorimetric method of determining molybdenum depends on this behavior.

Estimation.[1] For the analysis of molybdenum several methods are available for getting the material into solution. Fusion may be accomplished with Na_2O_2; with Na_2CO_3, K_2CO_3, and KNO_3 mixture; or with $KHSO_4$. The material may be decomposed with aqua regia, and if lead is present, sulfuric acid should be added and the mixture evaporated to dense fumes. Fusion with sodium peroxide is recommended as efficient and rapid. In the gravimetric determination of molybdenum it may be weighed as MoO_3,[2] which is prepared by the ignition of ammonium molybdate or MoS_3, or by the treatment of the latter with the nitric acid. In all such treatment care is necessary in the heating of MoO_3 since it is readily volatile at temperatures above 400° 450°. The complete conversion of the sulfide to the oxide requires long ignition and a carefully regulated temperature, which should not greatly exceed 350°. Molybdenum is sometimes determined as MoS_2 which is obtained by heating the precipitated MoS_3[3] in a stream of hydrogen. Reduction to constant weight requires much time. Another method involves the precipitation of mercurous molybdate from a neutral molybdate solution by a neutral mercurous nitrate solution. The yellow precipitate so obtained may be heated cautiously to expel mercury and the residue weighed as MoO_3; or the mercurous molybdate may be heated to dull redness in a stream of hydrogen producing MoO_2 or to white heat yielding metallic molybdenum; another plan is to heat mercurous molybdate with a weighed quantity of dry PbO until all the mercury is expelled, when the gain in weight is due to the MoO_3 retained by the lead. Both lead molybdate[4] and barium molybdate may be precipitated, dried, and weighed as such.

A small amount of molybdenum in tungsten may be determined by extracting molybdenum xanthate from a solution containing a little sulfuric acid by means of chloroform.[5] Trivalent arsenic may be separated from molybdenum by vaporization, partly as $AsCl_3$ and partly as $As(OMe)_3$ at the temperature of the water bath.[6]

Volumetric methods[7] for the determination of molybdenum are partic-

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[1] See Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*, pp. 162-170. Bur. of Mines, *Technical Paper* 230 (1920); *Min. and Sci. Press*, **117** 313.

[2] *Jour. Chem. Soc.* **114** (II) 244 (1918); *Jour. Soc. Chem. Ind.* **37** 561 A (1918); *Jour. prakt. Chem.* **97**, 154 (1918).

[3] *Zeit. anorg. Chem.* **110** 81 (1920); *Chem. Ztg.* **52**, 564; *J. Ind. and Eng. Chem.* **12** 998 (1920).

[4] *Jour. Chem. Soc.* **114** (II) 244 (1918).

[5] Dorothy Hall, *Jour. Am. Chem. Soc.* **44** 1462 (1922).

[6] Moser and Ehrlich, *Ber.* **55 B** 430 (1922).

[7] See *Compt. rend.* **165** 302 (1917); *Chem. Analyst*, **25** 9, 11 (1918) and **27** 23 (1918); *Can. Chem. Jour.* **2** 132 (1918); *Jour. Ind. and Eng. Chem.* **12** 578 (1920).

ularly acceptable because the gravimetric methods involving ignitions are difficult and tedious. A disadvantage in the use of volumetric methods is that they are reliable only in the absence of other metals. Consequently in the analysis of an ore, the molybdenum precipitates must be carefully purified. In Randall's method[1] a molybdenum solution is acidified with H_2SO_4 and passed through a zinc reductor into ferric sulfate solution, then the resulting ferrous iron titrated with permanganate. By a similar method molybdenum salts in acid solution may be reduced to the trivalent condition with zinc and titrated directly with permanganate or potassium iodate to the hexavalent state. By still another method the soluble molybdates in acid solution may be reduced to the pentavalent condition by boiling with KI and the free iodine titrated with thiosulfate; or, the free iodine may be boiled out, the solution made alkaline with $KHCO_3$, and the Mo^{+5} oxidized to Mo^{+6} by standard iodine or permanganate.[2] Titration with titanium chloride is commonly used in determining the molybdenum content of steels.[3] Sometimes ammonium molybdate is titrated with lead acetate solution in a manner just the reverse of the method used for determination of lead. This method is only applicable to samples containing considerable molybdenum because the end point in tannic acid solution is not sharp. In general, volumetric methods are more applicable when the ore is brought into solution by fusion.

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[1] D. L. Randall, *Am. Jour. Sci.* (IV) **24** 313 (1907).

[2] See *Zeit. anal. Chem.* **20** 507; *Ber.* **28** 2900; *Am. Jour. Sci.* (IV) **2** 156; *ibid.* **12** 449.

[3] M. Travers, *Compt. rend.* **165** 362 (1917).

CHAPTER XV

GROUP VI — TUNGSTEN[1]

Historical. — The name tungsten signifies "heavy stone" and calls attention to the high specific gravity of the element and its ores. These heavy minerals attracted attention long before their nature was understood. Agricola in his treatise on metallurgy (1556) refers to the mineral now known as wolframite as "lupi spuma," evidently, since this ore, which is frequently associated with tin, "eats up the tin as a wolf eats up the sheep." It is probable that the German names wolfram, wolfart, wolfort, etc., are traceable to the same notion, and from these come the modern names wolframite, wolfram, and the symbol of the element. Up to the middle of the eighteenth century these ores were considered to be compounds of tin. In 1781 Scheele proved that the mineral then called "tungstein," now known as scheelite, contained calcium and a new acid, which he called tungstic acid. He also proved that the mineral "tenn spat" (heavy spar or mineral), now called wolframite, contains the tungstate of iron and manganese. Bergmann during the same year became convinced that tungstic acid was the oxide of a metal. The Spanish chemists, the brothers d'Elhujar, studied the mineral wolframite in 1783-86 and produced for the first time the metal tungsten. They reduced the oxide with carbon and studied the alloys of tungsten with lead, silver, and gold. Tungsten was used as a constituent of alloy steels as early as 1855,[2] and other uses were suggested, but the development of the chemistry of this element was slow at first and up to about the beginning of the twentieth century it remained a scientific curiosity. The introduction of tungsten into the steel industry as a definite alloying substance created great interest in its chemistry, while the manufacture of ductile tungsten and its wide use in incandescent lamps has made the name a household word. There is probably no element of the whole periodic system whose chemistry has shown greater development in so short a space of time as has tungsten in the first twenty years of the present century.

Occurrence.[3] — Tungsten is rightly considered a rare element because it is found in only a few minerals. Quite fortunately its ores are found in some localities in fairly large quantities, generally associated with tin. The ores of commercial impor-

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[1] For an exhaustive bibliography of tungsten see *U. S. Geol. Survey Bull.* 666; also, *Bull.* 12, South Dakota School of Mines, pp. 164-236.

[2] Adolph Gurlt, *Trans. Am. Inst. Min. Eng.* **22** 236 (1893).

[3] See *Tungsten Bearing Ores*, U. S. Tariff Commission; also, Tariff Information Series, No. 21, pp. 290-318.

tance are of two general types, scheelite and wolframite. The former is calcium tungstate containing, when pure, 80.6 per cent WO_3, the commonest impurity being MoO_3, which is not an objectionable impurity for the manufacture of alloy steels, but is generally undesirable in making lamp filaments. The scheelite deposits are crystalline, white, yellow, or reddish in color, but never dark; the crystals are soft, easily scratched with a knife, and the specific gravity (6) is noticeably high, making mechanical separation easy.

Wolframite is essentially a tungstate of iron and manganese of varying proportions. Samples vary all the way from reasonably pure iron tungstate, known as ferberite, to relatively pure manganese tungstate, which is called hübnerite. As would be expected from the close relationship existing between iron and manganese, these two minerals resemble each other in all physical properties and can only be distinguished by chemical analysis. They contain practically the same percentage of WO_3 ($FeWO_4$ contains 76.3%, and $MnWO_4$ contains 76.6%). Technically samples of ore which contain more than 20 per cent FeO are called ferberite, while those containing more than 20 per cent MnO are known as hübnerite and intermediate materials are called wolframite. Practically, however, especially in the absence of accurate analyses, the term wolframite is used to cover all materials of this order. The mineral is either crystalline or granular in form, always dark in color, with a tendency toward brown in hübnerite and shining black in ferberite. The mineral is soft enough to be scratched with a knife, is very brittle, and shows perfect cleavage, breaking into thin, lustrous flakes. The specific gravity is about 7.5, equal to galena and greater than cassiterite, with which it is commonly associated in nature. Practically all the tungsten ore produced outside the United States is of the wolframite type.

Other forms of tungsten are found but usually more or less directly associated with the more common forms. Tungsten ochre is WO_3 and tungstite is its hydrated form; ferritungstite is a hydrated iron tungstate; all of these are minerals of a canary yellow color formed by oxidation and occurring chiefly as incrustations on deposits of scheelite or wolframite. There are also occasional samples of powellite, $Ca(MoW)O_4$, cuproscheelite, $(CuCa)WO_4$, and tungstates of copper and lead.

The world's principal supplies of tungsten have come from China, Burma, Japan, Australia, Bolivia,[1] and the United States, while smaller amounts have been mined in England, France, Germany, Portugal, Siam, and other countries. For some time the United States was the world's greatest producer of tungsten, but from 1913 to 1916, Burma produced the largest amount. In 1916, China produced 110 tons; in 1917, 1200 tons; and in 1918, 10,280 tons, the largest amount ever produced by any country. The Chinese deposits are in four provinces,[2] and the deposits are in the form of sands or pebbles in the streams or in small veins in granite rocks. Estimates of the ore in sight run as high as 100,000 metric tons. Most of the mining is done by hand labor, chiefly by farmers at odd times.

The Burma deposits cover an area 750 miles long, which not only supplies much tungsten, but also yields the greater part of the world's tin. The tungsten deposits have been known since 1846. The principal deposit is in the Tavoy region, which was lost for a time and rediscovered in 1909.[3] At present this district covers 5308 square miles of territory. Most of the wolframite is found in lodes which vary in thickness from a few inches to 5 feet and are known to extend as far as 2½ miles.

In the United States, nearly all the tungsten is produced in California and Colorado, with Arizona, Missouri, Nevada, New Mexico, and South Dakota producing small amounts. The California supply includes the largest scheelite deposit in the world, while Colorado has the highest grade ferberite deposits known. Production in these two states has been almost exactly equal during the past five or six years.

The world's total production in 1909 was 5250 metric tons of concentrate, containing 60 per cent WO_3. The production under the stimulus of war conditions rose rapidly, reaching a maximum in 1918 of 30,000 tons, of which China produced more than one third. Since 1918, production has fallen off materially, or ceased entirely, especially in countries where labor cost is high. The production continued for a time in the Chinese fields, though at a greatly reduced rate. For a time certain Colorado

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[1] See "Tungsten in South and Central America," *Chem. and Met. Eng.* **26** 698 (1922).

[2] C. Y. Wang, *Eng. Min. Jour.* **109** 16 (1920).

[3] *Jour. Soc. Chem. Ind.* **39** 44 T (1920).

tungsten plants, located within 50 miles of rich tungsten deposits, were enabled to run upon the cheaper Chinese ore.

Concentration of tungsten ores is almost invariably carried out at the mine and is easily effected by any method which takes advantage of high specific gravity. Usually the method of wet crushing and hydraulic classifiers is employed. On account of the brittleness of wolframite and its perfect cleavage, much of the ore is pulverized to such a fine state that the losses are heavy. Pyrite is removed from the concentrate by roasting and a magnetic separator, since wolframite is with difficulty rendered magnetic by roasting. It is, however, sufficiently magnetic to permit its separation in this manner from tin and other heavy minerals.

Under the stimulus of the wartime demand for tungsten, great improvements were made in the concentration of the ore, especially in the Boulder district,[1] which now is said to obtain the most efficient concentration of any locality in the world. The former heavy losses are decreased by substituting rolls for stamps, thus permitting the recovery of the coarse concentrates before the ball mill treatment; and by improvements in the "rag plant," which saves much tungsten formerly lost in the tailings. Attempts to use flotation and magnetic separation[2] have been made, but the results are somewhat discouraging.

That it is possible to concentrate tungsten successfully from a low grade ore under favorable market conditions is shown by the statements[3] that a certain 40-ton concentration plant in Colorado, working with mill feed averaging about one per cent WO_3, within four weeks from the day of starting, recovered the entire cost of the mill in the value of the products sold. Much yet remains to be accomplished in the milling of tungsten ores, however, since the average recovery is said to be about 70 per cent of the WO_3 contained in the ore.

In 1919, the New York price per unit of WO_3 was \$6.50-\$8.50 for Chinese ore, \$9-\$10 for Bolivian ore, and \$11-\$12 for Colorado ferberite. In December, 1921, the New York price was quoted at \$2.50-\$3 per unit of 60 per cent WO_3; in January, 1923, it was \$7.50-\$8.

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[1] S. Fischer, *Chem. and Met.* 16 559; 17 73 (1917).

[2] See also Hitchcock and Pond, *Min. Sci. Press*, 120 379 (1920).

[3] H. C. Parmelee, *Chem. and Met.* 14 301 (1916).

Extraction. — Several methods[1] are available for opening up tungsten ores, the choice depending on the nature of the ore, the impurities present, and the purpose of the extraction. These methods may be classified as follows: —

(1) Acid extraction, using either aqua regia or hydrofluoric acid. The former is suitable for high grade ores and concentrates, provided arsenic, phosphorus, and fluorides are absent. The latter is best adapted to low grade ores, especially those which contain decomposable silicates. These methods are used in analytical practice.

(2) Fusion with potassium bisulfate is satisfactory for ores containing arsenic and fluorides, but should not be used on ores containing phosphates. The melt is extracted with 5 per cent tartaric acid. On the large scale, this method has been recommended[2] for ores containing considerable tin. After fusion, the melt is extracted, first with water to remove soluble sulfates, then with warm ammonium carbonate solution. Tungsten forms in the fusion an acid potassium tungstate which is insoluble in the first extraction if sufficient excess acid is present, but is soluble in the carbonate extraction. Tin is recovered from the insoluble residue. This method requires a large excess of acid sulfate in the fusion.

(3) Digestion with caustic soda produces the soluble sodium tungstate, but it is not applicable to scheelite ores. There is also extracted with the tungsten more or less molybdenum, vanadium, arsenic, tin, aluminium, columbium, and tantalum.

(4) Scheelite ores[3] are easily decomposed by hydrochloric or nitric acid; or, they may be fused with potassium fluoride,[4] and the soluble potassium tungstate removed from the melt by leaching.

(5) Fusion with sodium carbonate, sodium peroxide, or sodium hydroxide likewise produces soluble sodium tungstate, molybdate, vanadate, etc. The caustic fusion method is adaptable to ores containing phosphates, fluorides, or titanium. The melt is extracted with water and on acidification tungstic acid is precipitated. Fusion methods are commonly used in large scale operations.

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[1] Schoeller and Powell, *Analysis of Minerals and Ores of Rarer Elements*, 177–182; Runner and Hartman, *Bull.* 12 So. Dak. Sch. Mines, 97–101.

[2] G. Gin, *Trans. Am. Electrochem. Soc.* **13** 481 (1908).

[3] H. Lavers, *Proc. Australian Inst. Min. and Met.*, 1921, No. 43, 101.

[4] G. Gin, *loc. cit.*

Of these methods the sodium carbonate fusion method is by far the most successful on a large scale, the other processes being chiefly serviceable for analytical purposes. As carried out on wolframite containing[1] 1 per cent tin, .05 per cent copper, and a small amount of silica, the ore is crushed and fused with 15 per cent excess of sodium carbonate to which some sodium nitrate is sometimes added. A typical reaction is: $2\ FeWO_4 + O + 2\ Na_2CO_3 = 2\ Na_2WO_4 + Fe_2O_3 + 2\ CO_2$. After heating two hours at 800° C. in a reverberatory furnace during which the mass is rabbled by hand, the melt is drawn off into pans, cooled, and crushed. The soluble tungstate is dissolved in water and is sometimes recrystallized. Then the acid may be precipitated by acidification; or an excess of $CaCl_2$ is added, causing the separation of $CaWO_4$, which is thoroughly washed. When hydrochloric acid is added and the material heated to boiling, H_2WO_4 separates as a yellow mass. This material contains as impurities small amounts of lime, silica, iron, and alumina. To remove these it is washed, filtered, and converted to ammonium paratungstate, $(NH_4)_6W_7O_{24}$, by adding water and NH_4OH, and filtering off any residue. The ammonium salt is evaporated and the residue dried and treated with HNO_3. The tungstic acid so formed is again dissolved in ammonia and the process repeated. Finally the acid is heated in fused silica ware at 1000°, when WO_3 is obtained as a powder, the color varying from pure yellow to dull green, depending on the purity. Finally a purity of 99.97 per cent is reached, and most of the remaining impurities are removed during the reduction process. The oxide is obtained in the form of a powder, the coarseness of which may be controlled by regulation of the time and temperature of ignition and the purity of the material. The physical condition of the powder is of great importance since it determines in large measure the working properties of the metal obtained from it.

A method of decomposing tungsten ores and forming WO_3 directly has been suggested.[2] By this method the finely ground ore is mixed with carbon and heated to 300° in a stream of dry chlorine. The chlorides or oxychlorides of tungsten distill out

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[1] At the Fansteel Plant, North Chicago; see C. H. Jones, *Chem. and Met.* **22** 9 (1920).

[2] British Patent, 134,891.

of the mixture. The oxide is produced by hot water or by heating in a stream of air which carries away the chlorine.

Metallurgy. — Tungsten may be obtained in metallic form by several methods: (1) the oxide may be reduced with hydrogen, carbon, zinc, aluminium,[1] or magnesium; also, by silicon carbide, boron, and silicon;[2] (2) reducing the chloride with hydrogen; (3) heating the nitride; (4) electrolysis of the double sodium tungsten chloride. Of these processes only the first two are of commercial importance.

Reduction with carbon is accomplished by heating dry WO_3 with a slight excess of carbon in closed crucibles at a temperature of 1400° C. At the end of the operation the metallic powder contains excess carbon and some unreduced oxide. To remove these the mass is elutriated with water, and the material so removed used in the next charge. A purity of 98 per cent may be realized by this method, but the product always contains carbon as an impurity, which renders the metal too brittle for mechanical working. It is, however, suitable for use in making alloy steel and is cheaper than the metal obtained by reduction in hydrogen.

Reduction of WO_3 with pure hydrogen yields a very pure metal suitable for tungsten products or drawn tungsten, but the process requires skill and care. The process is successfully carried out by putting the oxide in long, shallow nickel trays and placing these in quartz tubes which are heated by electrical resistance. The temperature must be raised gradually in order to prevent fusion of the oxide before the reduction starts. If the material fuses, only superficial reduction takes place. The temperature required is about 1200°, and about 7 hours are needed to effect complete reduction. Upon removal from the furnace the tungsten is in the form of a gray powder, whose apparent density varies from 1.2 to 6.0, depending largely upon the density of the WO_3 used. The powder is then placed in a mold and subjected to a hydraulic pressure of 30–100 tons per square inch of surface. This forms fragile bars or ingots in which the individual particles are held together mechanically. In the next step, called baking, these ingots are toughened by a preliminary heating in hydrogen in an electric furnace which is kept at

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[1] *Elecktrochem. Zeit.* **26** 29 (1920).

[2] F. M. Becket, U. S. Pats. 858,328; 854,018; 930,027; 930,028.

about 1300°. After this process the bars may be handled without danger of breaking, but they are still porous, containing about 40 per cent voids.

In the next process, the bars are sintered by heating electrically between tungsten electrodes in an atmosphere of hydrogen. The flow of the low voltage current used is so regulated that a temperature of approximately 3200° C is obtained. This temperature is sufficient to cause the individual particles of tungsten to adhere to one another, but extreme care is needed not to fuse the metal, since the fused metal is highly crystalline, brittle, and impossible to work. During the sintering process, crystals begin to form, small at first, but increasing in size as the process is continued. This phenomenon is called technically "grain growth," and as it continues the voids disappear, the bar shrinks in size, and becomes very hard, and shows definite metallic properties, but it is still quite brittle. If sintering is continued too long, or too high a temperature is used, the crystals become too large, producing a brittle product which cannot be worked.[1] It is easily seen that the size of grains in the tungsten powder has a marked influence upon the process of grain growth, and hence is an important factor in determining the properties of the metal produced by the sintering.

In the next process, which is called "swaging," the tungsten ingots are heated to about 1600° in an atmosphere of hydrogen, then placed in a machine which is fitted with a rapidly revolving shaft, carrying a die, the size of which may vary. As the shaft revolves, small hammers are driven against the heated tungsten, several thousand blows per minute being distributed regularly over the surface of the bar. In this manner the diameter of the bar is reduced about 4 per cent during each treatment. By changing the die to a slightly smaller size the tungsten is worked down to the desired diameter. As the swaging continues the temperature is gradually reduced to about 800°, and as the bar elongates it is found that the crystals themselves become longer and longer. As this process continues the metal becomes more and more ductile at room temperature. If ductile tungsten is desired, the swaging is continued until a diameter of about

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[1] See Jeffries, *Bull. Am. Inst. Min. Eng.* No. 119, 2065 (1916); Jeffries and Archer, *Chem. and Met. Eng.* 27 789 (1922); Smithells, *Jour. Inst. Metals*, 27 107 (1922).

0.75 mm. is obtained, when the wire is sufficiently ductile at room temperature to permit cold drawing and working.

If a rod of tungsten, which has become ductile at room temperature through the elongation of its crystals, is heated for a short time to a sufficiently high temperature, the long crystals are changed to equiaxed crystals and the metal once more becomes brittle at ordinary temperatures. In such a condition it cannot be worked except at high temperatures. The temperature at which the elongated crystals change to equiaxed crystals is called the equiaxing temperature, and this temperature becomes lower as the elongation through working increases. Thus a rod which has been worked until it shows a 24 per cent reduction in area is equiaxed by exposure to a temperature of 2200° C. for 5 minutes. But if the reduction in area has reached 99.99 per cent, the wire is equiaxed at about 1350° in 5 minutes or less. A longer exposure to a lower temperature produces similar results. In the equiaxed condition tungsten is brittle at room temperature, but it becomes very dutcile when heated to higher temperatures. It will be recalled that when the common ductile metals have become brittle through mechanical strain at moderate temperatures, they readily recover their ductility when heated to the annealing or equiaxing temperature. Consequently, most metals are in their most ductile form when they are composed of small equiaxed grains. On account of the fact that equiaxed tungsten is brittle *at room temperature,* some metallographers contend that tungsten behaves in a manner which is directly opposite to such metals as gold, silver, and copper. On the other hand, other workers point out that tungsten at room temperature is very much farther below its melting point than the other metals; that when heated it becomes extremely ductile at temperatures far below its equiaxing temperature, and hence it must be considered a very ductile metal, when the difference in melting point is considered. According to this view equiaxed tungsten is in its most ductile form if the metal is worked at the proper temperature. The question of the ductility of tungsten is the basis of the present tungsten patent situation, and important litigation has centered around this point.

Ductile tungsten in the form of fine wire may be prepared by cold drawing, but usually this process is also carried out at somewhat elevated temperatures. The temperature used varies from 400° to 650°, depending on the size of the wire. The drawing is done through a cylindrical block in which the diamond is fixed. The size of the die is reduced very gradually, at certain stages the interval is reduced by as little as 0.00125 mm. Thus a very large number of dies are needed, since the wire may be as fine as 0.005 [1] mm.

In the preparation of lamp filaments it has been found desirable to introduce 0.75 per cent ThO_2, before the WO_3 is reduced. The thorium oxide appears in the final product as small globules, whose presence influences the direction and degree of grain growth, giving a tougher filament.

Ductile tungsten has also been produced by electrolytic deposition.[2] If WO_3 is dissolved in boric acid at 1200°–1400°, the solution may be electrolyzed, the deposited tungsten being sufficiently ductile to permit drawing through dies of high speed steel lubricated with talc.

Methods have recently been described [3] for preparing tungsten filaments out of a single long crystal which will not equiax. Hence it is claimed that the wire is more flexible, ductile, and has a longer life than filaments of drawn tungsten. The long crystals are made by preparing very fine metallic tungsten, a definite amount of ThO_2 is then added and the mixture made into a paste with a small amount of a colloidal binding material. A filament is formed by squirting this paste through a fine opening. These are dried at a moderate temperature, placed in a cylinder of reducing gas, and run through a furnace at a rate equal to the advance of the crystal face. If the heating is done properly, in place of having a series of small crystals which are liable to break at their interfaces, one long crystal is obtained which is said to be softer at low temperatures and harder at high temperatures than drawn tungsten. Crystals 25 inches long have been prepared in this manner. A comparison under similar conditions after 1200 hours' burning showed that the single crystal had not vaporized at all, while the lamp containing the drawn filament showed a material deposit.

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[1] Such a wire is roughly one fifteenth the size of a human hair and has a diameter about equal to that of a spider web. The finest gold thread reported, 3240 meters of which weighed one gram, had a diameter of about 0.0046 mm.

[2] *Eng. Min. Jour.* July 27, 1918, p. 163.

[3] *Jour. Ind. and Eng. Chem.* **10** 574 (1918); *Zeit. Ver. deut. Ing.* **62** 15 (1918).

Properties. — The properties of tungsten show material variation, depending on the degree of purity and the methods of production and treatment. The following statements are taken from some of the best recent publications and refer for the greater part to the ductile form of the metal.

The density varies from 19.3 to 21.4, about 70 per cent more than lead. The tensile strength runs from 322 to 427 kilograms per square millimeter, approximately a third more than that of iron.[1] The elastic modulus is 42,200 kilograms per square millimeter, fully twice as great as steel. Coefficient of expansion is 43×10^{-6}, the specific heat 0.0358, the hardness 4.5 to 8.0 on Moh's scale, one of the hardest of all metals. It has the highest recrystallization temperature after strain hardening of all known metals. When a wire is composed of small equiaxial grains it is extremely brittle at room temperature, but when the structure is fibrous in nature the wire is ductile and pliable at ordinary temperatures. The electrical resistance at 25° varies between 5.0 and 6.2 microhms per cubic centimeter. Its ductility is so great that it may even surpass gold in this respect. It has the lowest vapor pressure and the highest melting point of any metal; its melting point is probably exceeded by only one element, carbon. Melting point determinations vary from 2800° C. to 3350° C.,[2] the value 3267° C., given by Langmuir, being probably the best yet obtained. Fink gives the boiling point around 3700° C.

In powdered form, the metal is hard, brittle, and crystalline and finds few applications. In the compact or ductile form it is much softer and tougher. It may be rolled into sheets, but it cannot be welded at any temperature at which it is worked.

At ordinary temperatures it is entirely unaffected by air or water, but at elevated temperatures it oxidizes readily. Molten sulfur and phosphorus attack the metal slowly, while the vapors of these elements react with it vigorously. The metal is not attacked by alkaline solutions, but fused nitrates, peroxides, alkaline carbonates, hydroxides, and acid sulfates attack it

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[1] It is obvious that the tensile strength of tungsten varies enormously with its condition and treatment. See Z. Jeffries, *Bull. Am. Inst. Min. Eng.* 1918, p. 1041. A ductile tungsten wire of about .03 mm. diameter has 33 times the tensile strength of the sintered bar from which it was prepared. In working with other metals a sixfold increase in ductility is unusual.

[2] *Eng. Min. Jour.*, July 27, 1918, p. 163.

readily. Sulfuric and hydrochloric acids have no effect, except when boiling hot and concentrated, when the action is slow. Nitric and hydrofluoric acids have little or no action separately, but a mixture of these two acids is a good solvent for tungsten.

The application of a temperature of 20,000° to fine tungsten wire appears to decompose the heavy atoms of tungsten and to liberate helium.[1]

Uses. Tungsten finds a great variety of uses, which may be classified as follows: (a) electrical contrivances, (b) lighting devices, (c) miscellaneous uses of the metal and its compounds, (d) non-ferrous alloys, and (e) the steel trade. Of these the latter takes by far the largest amount of tungsten, while tungsten incandescent lamps are the best known and the other uses indicate the possibilities of a greatly increased demand for this interesting metal.

Tungsten contact points are widely used in spark coils, voltage regulators, telegraph keys, and similar devices in place of the platinum or platinum-iridium formerly considered essential. During the war time shortage of platinum, great interest was shown in tungsten points, and they are now regarded as superior to platinum because of the higher vaporization point, the greater hardness, and a heat conductivity which is twice that of platinum.[2] The cost is much below that of the platinum points. In preparing these tungsten contact points great care is necessary to develop uniform hardness throughout, in order to prevent, as far as possible, the pitting of the points. These contact points are stamped out of sheet tungsten, or a wire of the desired diameter is prepared as already described. This is then cut into proper lengths by a rapidly revolving wheel, which is made of vulcanized rubber in which carborundum is imbedded. These wheels may be 0.25 mm. in thickness and about 3 or 4 inches in diameter, and while they are cutting the tungsten they are cooled by a suitable liquid. The tungsten buttons made in this way are brazed on to the steel holder by means of a thin copper disk. The whole arrangement is heated to a temperature which vaporizes the copper, causing it to permeate both the steel and the tungsten and thus firmly brazing the two together. In

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[1] Anderson, *Astrophys. J.* **51** 37 (1920); Wendt and Irion, *Jour. Am. Chem. Soc.* **44** 1887 (1922).

[2] *Trans. Am. Inst. Elect. Eng.* **31** 870

this manner the contact screw is mainly steel while the exposed end is a button of tungsten.

Tungsten wire forms an excellent material for winding electric furnaces, on account of the very high temperature which may be obtained. Temperatures as high as 1600°–1800° C. may be maintained by this means,[1] although at high temperatures the wire must be carefully protected from oxygen.

Tungsten buttons brazed to copper form an excellent anticathode in the Roentgen tubes, because of the high specific gravity, high heat conductivity, high melting point, and low vapor pressure.

Tungsten electrodes are efficient in certain electrochemical processes where the resistance to corrosion is a great factor.

Tungsten-molybdenum thermocouples are useful, especially at high temperatures. They give an increase in electromotive force with an increase of temperature up to 540° C. and pass through zero millivolts at 1300° C.

Sheet tungsten has played an important part in the recent marked advances in wireless telegraphy and telephony, since it is found to be a very efficient metal for the construction of the amplifier. The manufacture of sheet tungsten presents some difficulties and has only recently been successfully performed. The swaged bars are heated in hydrogen to 1200°–1400° C. and then rolled to the desired thickness. Much care must be used to prevent overheating, since this causes recrystallization. The rolled sheets have a tensile strength as great as 500,000 pounds per square inch.

In lighting devices tungsten is used both as an incandescent filament and as a pencil in arc arrangements. It yields a brilliant light, especially in its arc, which is rich in actinic rays, serviceable in projection, and ultra-microscopic work.[2] A tungsten arc, called by the trade name of "pointolite," has found some use in England. It is said to consume about 0.4 watt per candle power. Tungsten arcs have also been used in an attempt to find an arc in which the illumination came from the surrounding gas and not from the electrodes.[3] The most successful results were obtained by sealing tungsten electrodes in a resistance

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[1] *Trans. Am. Electrochem. Soc.* **20** 287 (1911).

[2] *Elektrotech. u. Machinebau.* **36** 345 (1918).

[3] W. A. Darrah, *Trans. Am. Electrochem. Soc.* **29** 625 (1916); *Chem. and Met.* **13** 915 (1915).

glass bulb with an atmosphere of $TiCl_4$ or $TiCl_2 \cdot Br_2$. An efficiency as high as 0.25 watt per candle power was obtained and the electrodes require little attention, so this method of illumination appears to be promising.

Tungsten is so efficient and so widely known as a filament for the incandescent lamp, that it may be said that the entire industry of incandescent electric lamps depends upon this element. The industry began[1] with the carbon filament which for many years was the only material used. The first metal filament was made of osmium and was introduced by Welsbach in 1898. These lamps never became popular because of the high cost, the fragile nature of the filament making a vertical position necessary, and the fact that only low voltage lamps were possible.[2] But they did a great service in that they indicated the direction in which improvements were to be expected. The first metal filament lamp which was successful commercially was introduced by Siemens-Halske in 1903. It contained a tantalum filament, which permitted the production of a lamp of any ordinary voltage. On account of the fact that tantalum has a much lower specific resistance than carbon, the metal filament has to be two and a half times as long and one quarter the diameter of the carbon for equal voltage and candle power. Another difficulty came from the fact that at the incandescent temperature tantalum is very near the softening point, hence, a long loop or coil is impossible. These difficulties were overcome by divising the so-called " spider " arrangement, familiar in the later tungsten lamps. This permitted the lamp to burn in any position. These lamps quickly became popular, and between 1905–1911 about 103,000,000 lamps were sold.

In the efforts to produce an efficient tungsten filament many methods were attempted, such as squirting a mixture of tungsten powder with a binder through a small opening and heating the filament, squirting a tungsten amalgam or other alloy, then vaporizing the alloying metal. Some success was met in preparing a filament by squirting colloidal tungsten, which is sufficiently coherent to make a binder unnecessary. But the real success of the tungsten filament came with the introduction of the drawn wire filament. The first lamps were evacuated

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[1] See Johnstone, *The Rare Earth Industry*, pp. 73–89.

[2] F. G. Bailey, *Electrician*, **52** 646 (1904).

to prevent the oxidation of the metal, but the invention [1] of the nitrogen-filled lamp marked a decided advance. This has been followed in turn by the argon and neon lamps for special purposes. Table XXXV gives data for comparing the efficiency of various lamp filaments. The values given represent a fair average and are interesting for comparison. The advantages found in the tungsten bulb filled with an inert gas are that the metal vaporizes much less than in an evacuated bulb and that loss of heat is also less. Hence, longer life and greater efficiency result, while a material advantage, especially in stores, is that colored goods appear much more nearly true to their daylight colors than with almost any other means of artificial illumination.

TABLE XXXV

Comparison of Various Incandescent Filaments

	Watts per Candle Power	Candle Power per Square Millimeter	Temperature of Incandescence Centigrade	Ratio of Hot to Cold Resistance
Carbon	3.5	0.154	1800	0.5
Carbon metallize . .	2.5	——	——	——
Osmium	1.5	0.331	1900	8.94
Tantalum	1.6	0.307	1700	6.07
Tungsten (drawn) .	1.15	0.441	2150	12.12
Tungsten (squirted) .	1.25	——	——	——
Tungsten (N.-filled) .	0.5	——	——	——

The production of tungsten lamps has increased at an enormous rate. In 1907 tungsten filaments were found in about one lamp in a thousand in the United States. In 1918 tungsten lamps comprised 89 out of 100,[2] while the carbon lamp had disappeared from the general market. In 1914 the total production of tungsten lamps in the United States was 100,000,000, requiring about 3 tons of 60 per cent concentrate. Two years later the production had doubled.

Many applications for tungsten have been suggested because of its ability to resist corrosion of acid and alkaline liquors, such as gauze in centrifugal machines, frames and supports for filter

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[1] Langmuir, *Proc. Am. Inst. Elect. Eng.* (1913) p. 1915; *Trans. Illum. Eng. Soc.* **9** 775 (1914).

[2] *Gen. Elec. Rev.* **22** 767 (1919).

presses, utensils[1] in acid plants, and scientific instruments which are exposed to vapors. Numerous other uses have been suggested, such as cross hairs in telescopes and galvanometer suspensions, where fineness and high tensile strength give it a decided advantage; metal strings in musical instruments, where strength, elasticity, and resistance to climatic effects are important; springs for electric meters and watches, where its nonmagnetic properties make it useful; pen points, useful because of its elasticity and resistance to corrosion. It is also suggested[2] as a catalyst in the production of ammonia from nitrogen of the air. Tungsten would be an ideal material from which to fashion standard weights if it were possible to devise a method of shaping the pieces and adjusting their weights.

Compounds of tungsten are also used for a variety of purposes. The oxide is used in ceramics to produce various shades of yellow in glass and porcelain.[3] Sodium tungstate is used to decolorize acetic acid and fireproof cloth, as well as for a mordant and weighting material for silk. Considerable fluorescent calcium tungstate is used for making intensifying screens for X-ray photography, while cadmium tungstate is used for making the fluorescent screens for visual observation in X-ray practice. Tungsten carbide has a hardness of 9.8 and has been suggested[4] as a substitute for diamond in dies and drills as well as for bearings. The so-called tungsten bronzes are made by fusing together an alkali tungstate and pure tin. These form various shades of red, yellow, or blue which are used for decorative purposes.[5] They are usually regarded as compounds of the tungstates with tungsten dioxide, somewhat similar in nature to tungsten blue. (See Intermediate Oxides of Tungsten.)

Tungsten has a marked effect on the properties of alloys, consequently a great variety of alloys have been prepared. The usual effect of tungsten is to produce hardness and greater resistance to oxidation and corrosion. Some tungsten alloys are said[6] to be actually harder than diamonds. Aluminium hardened with a small per cent of tungsten, called "partinium,"[7]

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[1] Brit. Pat. Mar. 8, 1917; also U. S. Pat. 1,318,452.

[2] U. S. Pat. 1,175,693.

[3] A. Granger, *Compt. rend.* **140** 935 (1905).

[4] *Elektrochem. Zeit.* **26** 29 (1920).

[5] E. Engels, *Zeit. anorg. Chem.* **37** 125 (1903); Schaefer, *ibid.* **38** 148 (1904).

[6] *Elektrochem. Zeit.* **26** 29 (1920).

[7] J. H. Pratt, *Min. World*, Dec. 3, 1904.

is both light and strong and is used in France for automobile construction. "Sideraphite"[1] is an alloy of tungsten with iron, nickel, aluminium, and copper, which resembles silver in appearance, is ductile, malleable, and resistant to corrosion. The alloy "platinoid" contains copper, zinc, nickel, and tungsten; both platinoid and partinium are used, as well as ferronickel, for sealing into the glass of electric light bulbs, because their coefficient of expansion is the same as glass. Some tungsten alloys are suggested for jewelry — an alloy containing 75 per cent gold, 10–15 per cent tungsten, and 15–10 per cent nickel is easily rolled or hammered and takes a finer polish than platinum; a similar alloy, in which silver replaces gold, is strong, resists oxidation, and takes a beautiful polish. The aluminothermic process has been used[2] to some extent in the production of tungsten alloys.

The most important non-ferrous alloy of tungsten is the alloy called stellite.[3] This alloy is exceedingly hard, quite brittle,[4] silvery white in appearance, is unaffected by any but the strongest acids, and has found applications in widely different fields. It is efficient in cutlery, because it takes and holds a keen cutting edge, and does not tarnish even on contact with the most acid fruit juices. It has, also, given satisfactory results when made into pen points for fountain pens. The tips are made of hard stellite, welded to the malleable alloy, giving long service and freedom from corrosion. It is used for dental and surgical instruments, wood-working tools, and cold chisels, but its greatest use seems to be as a high speed lathe tool. A test made in boring automobile cylinders in the inventor's factory[5] showed that more than twice as many cylinders could be turned out in a day with a stellite tool as could possibly be bored with high speed steel tools. General adoption of such tools is delayed by the high cost, which is excused by the manufacturers on the ground that the tools cannot be forged, but must be cast and ground down, which makes the cost of manufacture high.

Ferrotungsten is by far the most important alloy of tungsten,

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[1] J. H. Pratt, *Min. World*, Dec. 3, 1904.

[2] *Iron Age*, July 25, 1918, p. 238.

[3] See Elwood Haynes, *Trans. Am. Inst. Min. Eng.* **44** 576 (1912); *Trans. Am. Electrochem. Soc.* **37** 507 (1920).

[4] A. J. Langhammer, *Chem. and Met. Eng.* **22** 830 (1920).

[5] Elwood Haynes, *loc. cit.*

and it has been estimated that normally 90–95 per cent of the tungsten mined finds its way into the steel trade. It is to be observed that in tungsten steel very considerable quantities of tungsten are required, while in all other uses a small quantity of the metal is sufficient.

The manufacture of ferrotungsten was formerly controlled by German interests, but, with the intense demands of the war, numerous reduction plants were built in the United States, England, and France. At the close of 1918 there were 20 producers of ferrotungsten and tungsten powder, with an estimated[1] normal consumption of 7500 tons of 60 per cent concentrate annually. These new plants generally produce ferrotungsten by the electric furnace method.

Various methods are available for producing this alloy, such as the reduction of the ores by aluminium[2] or ferrosilicon,[3] but previous to 1900 ferrotungsten was made almost wholly by mixing the ore with iron and a suitable flux and reducing with carbon in clay lined crucibles in a gas fired furnace. Since 1900 the electric furnace production has increased in favor and is now about the only method used. Reduction of ores of the wolframite type with carbon is easily accomplished[4] in the electric furnace, but scheelite ores give trouble because of the sticky, basic slags formed. An alloy containing 75–80 per cent tungsten can be produced, and low run wolframite ore can be used. The alloy is not tapped since its melting point is too high, but is allowed to accumulate to the end of the run, about 30 hours. As produced in this manner the alloy contains more carbon than is desirable for steel making, and a common practice[5] is to decarbonize by heating for 10–20 minutes after reduction is complete with a slag of iron ore, lime, and fluorspar. This causes a loss of 8–10 per cent tungsten, but the carbon content is considerably lowered. The average American specifications[6] are: W not less than 70 per cent; C not more than 0.6 per cent; S = 0.06; P = 0.07; Si = 0.6; Mn = 0.6; CaO = 0.5, and usually no copper or tin. Probably the most common harmful

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[1] E. J. Anderson, *Trans. Am. Electrochem. Soc.* **37** 275 (1920).
[2] A. J. Rossi, *Min. Ind.* **11** 693 (1902).
[3] G. Gin, *Trans. Am. Electrochem. Soc.* **13** 481 (1908).
[4] J. G. Dailey, *Raw Material,* **2** 67 (1920).
[5] R. M. Keeney, *Trans. Am. Electrochem. Soc.* **24** 127 (1913).
[6] C. G. Fink, *Min. Ind.* **28** 707 (1919).

impurities[1] in ferrotungsten are copper, tin, manganese, phosphorus, and sulfur. Methods have been suggested[2] for improving ores containing these impurities, but usually the ores are purchased on specifications which are determined by the use to be made of the product.

The loss of tungsten in the production of ferrotungsten has been estimated by the Bureau of Mines as between 14 and 25 per cent. These losses are largely mechanical, but are partly due to incomplete reactions.

Tungsten steel has become one of the most valuable of steel products, since by its use in the machine shop each machine is able to turn out five times as much work in a day as was possible with carbon steel tools. The importance of tungsten steel as a war material is emphasized by the fact that one authority states that tungsten is a war essential of fundamental importance, surpassed among the metals only by iron itself. Great Britain put tungsten second in the list of contraband of war. The United States has been the greatest user of tungsten, as shown by the fact that although this country has been one of the leaders in the production of tungsten, since 1917 considerably more than half of the domestic requirements have been met by foreign tungsten supplies.[3]

The addition of tungsten to steel has the effect of increasing hardness, toughness, tensile strength, and elasticity. The most remarkable property doubtless is that of red-hardness, which means that the steel retains its hardness even when it is hot. This permits a tungsten steel cutting tool to be used at a speed 3–6 times that possible with a steel whose hardness depends on its carbon content. As a result of this fact this material has come into almost universal use in machine shop practice for cutting tools. In addition, tungsten steel possesses properties which make it valuable in the manufacture of ignition parts of internal combustion engines. It has been found especially satisfactory for engine valves and seats of airplane engines. It is also used in making automobile parts, armor plate, heavy ordnance, projectiles, magnets, saw blades, and various other uses.

Tungsten steels are made either with the powdered metal or

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[1] *Bull.* 652, U. S. Geol. Survey.

[2] W. Baughman, *Min. Sci. Press*, **114** 800 (1917); *Eng. Min. Jour.* **98** 16 (1914).

[3] Tariff Information Series, No. 21, p. 279 (1920).

with ferrotungsten. The use of the latter seems to be growing rapidly, and may eventually become the universal practice. About half the tungsten steel now made is prepared by the use of the ferro alloy.[1] The advantages claimed for it are that it mixes better on account of its lower melting point, and there is less loss by oxidation than when the powder is used. It is obvious that a uniform ferrotungsten is essential if results are to be definitely controlled. The steels are made either by the crucible process or in the electric furnace. The latter is claimed to give a superior product because it permits a better control of the chemical composition.[2] The tungsten is added on the top of the charge, and care must be exercised to get an even distribution and prevent settling of the heavier tungsten.

Simple tungsten steel[3] contains no alloying element except tungsten, which is usually present in amounts from 3–6 per cent, while the carbon runs about 0.6 per cent, though as much as 1.0 per cent C is common. Such steels must be hardened by quenching; they are used chiefly for manufacturing permanent magnets, for electric meters and hand dynamos, and finishing tools for lathe work.

Most tungsten steels contain other alloying constituents, especially the high speed, or rapid, steels. Chromium, vanadium, cobalt, nickel, molybdenum, and many other metals are used along with tungsten for certain specific purposes. The per cent of carbon runs usually from 0.5 to 0.75, manganese less than 0.5, but the amount of tungsten is quite commonly 12–15 per cent, while 18–20 per cent or more is used. Generally the effect of molybdenum is to reduce the quantity of tungsten required to give a desired effect. Vanadium is an important factor, the amount varying from 0.5 to 2.5 per cent or more. Chromium is considered an important factor in producing hardness, and it is present in amounts from 2–6 per cent, though some European steels contain as much as 9 per cent of this element. Tool steel of this type requires careful and skillful heat treatment, which commonly consists of heating to incipient fusion and quenching in oil or melted lead. Cooling by air blast is used, but produces surface oxidation.

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[1] R. J. Anderson, *Trans. Am. Electrochem. Soc.* **37** 276 (1920).

[2] R. C. McKenna, *ibid.* **37** 319 (1920).

[3] U. S. Bureau of Mines, *Bull.* 100.

Since the addition of tungsten increases the weight of steel uniformly, the percentage of tungsten may be determined with some accuracy by the specific gravity alone, provided other elements are constant.[1]

Compounds. — The compounds of tungsten resemble those of molybdenum very closely. It exists in several states of oxidation, the lower forms being more or less unstable and the forms from the highest oxide, WO_3, being by far the most important. The most important tungsten compounds are those formed when WO_3 is acting as an acidic oxide. The alkali tungstates are generally soluble in water while the heavy metal tungstates are not. Table XXXVI indicates the relationship between the various classes of tungsten compounds. The compounds of lower valence are produced by reduction and are as a rule of little importance. Reducing agents produce a series of colors, similar to those obtained by the reduction of molybdenum. It is to be observed that as the valence of tungsten increases from two to five, there is, also, some slight increase in basicity, at least so far as permanence and character of the compounds is concerned. This is directly opposite to the facts observed in the case of nearly all other elements. In spite of this apparent peculiarity, tungsten in its highest state of valence is mainly acidic. Bivalent tungsten is known only in simple compounds with the halogens; in the trivalent condition tungsten forms double chlorides with the alkali metals; quadrivalent tungsten forms halides and double cyanides, besides the oxide, sulfide, and selenide; pentavalent compounds include simple halides and oxy-salts, cyanides, sulfo-cyanides, and oxalates; hexavalent tungsten forms halides, oxy-halides, sulfides, oxysulfides, in addition to the numerous and important derivatives of the oxide.

Tungsten resembles molybdenum in showing a remarkable ability to form complex compounds. One molecule of an alkali oxide may be combined with 1, 2, 3, 4, 5, 6, or 8 molecules of WO_3; while more complex molecules may contain as much as $5M'_2O$ condensed with varying amounts of WO_3. There are also formed many series of complex tungstates in which WO_3 combines with varying proportions of the oxides of silicon, phosphorus, arsenic, antimony, vanadium, and boron.

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[1] Townsend, A. S., *Trans. Am. Soc. Steel Treat.* **2** 133 (1921).

TABLE XXXVI

Compounds of Tungsten

VALENCE	OXIDE	HYDROXIDE	NATURE	TYPICAL SALTS	CHARACTERISTIC COLOR	CLASS NAME	REMARKS
W^{II}	—	—	Basic	WCl_2	Gray (brown solution)	Dihalide	Oxidized in air
W^{III}	—	—	Basic	$K_3W_2Cl_9$	Yellow to green	Double chloride	Double salts only
W^{IV}	WO_2	—	Basic	WCl_4, WS_2 $W(CN)_4 \cdot 4\,KCN$	Grayish	Tetrahalide; disulfide	Hygroscopic; slightly hydrolyzed
W^{V}		$W(OH)_5$ (?)	Basic	WCl_5, $WOCl_3$ $W(CN)_5 \cdot 3\,KCN$	Green-black	Pentahalide	Very hygroscopic: hydrolyzed by much water
W^{VI}	WO_3	$WO_3 \cdot H_2O$ $x\,WO_3 \cdot H_2O$	Basic	WCl_6, $WOCl_4$ WS_3	Red	Hexahalide	Unchanged in air; decomposed by boiling water
			Acidic	H_2WO_4 $H_2W_4O_{13}$ $H_{10}W_{12}O_{41}$ $x\,H_2O \cdot y\,WO_3$	Yellow Yellow	Normal tungstic Metatungstic Paratungstic Polytungstic	Alkali salts soluble Salts soluble Salts soluble Great variety

Oxygen forms two well-defined oxides, WO_2 and WO_3. Many other oxides are reported, but the existence of such formulæ as WO, W_2O_3, W_4O_3, W_5O_9, W_5O_{14}, W_3O_8 is probably best explained as a mixture of the element with varying amounts of a definite oxide, or as compounds of WO_2 and WO_3 similar to the intermediate oxides of molybdenum. (See p. 259.) The oxide prepared by the ignition of ammonium paratungstate is green. The color is usually explained as being produced by the reduction of part of the yellow oxide to the blue stage. This reduction may be caused by dust or organic matter and is catalyzed by light.[1]

Tungsten dioxide is prepared by reducing WO_3 with hydrogen or by hydrolysis of WCl_4. It is a heavy powder of red or brown color, strongly pyrophoric and easily oxidized to the hexavalent state. It may be obtained as small octohedral crystals, which are permanent in the air and insoluble in HCl. The amorphous form is more readily acted upon both by air and by acids.

Tungsten trioxide is found in nature and may be prepared by heating tungstic acid,[2] the metal, the lower oxide, or the sulfide. It generally forms a yellow amorphous powder, but may be obtained in crystalline form; it is insoluble in water, but the hydrate is soluble. It is difficultly fusible, but when heated in hydrogen, it is gradually reduced, yielding the blue oxide at 250°, WO_2 at red heat, and later the metal itself. It is insoluble in all acids except hydrofluoric, but dissolves readily in ammonia and the alkalies.

Intermediate oxides of tungsten are formed by the partial reduction of WO_3 or the tungstates, giving a material commonly known as tungsten blue. The reduction may not form a single definite compound, since the reduction is continuous from WO_3 to WO_2 or even to metallic tungsten. Many formulæ have been proposed for this blue product, such as W_2O_5,[3] W_3O_8,[4] W_4O_{11},[5] $W_5O_{14} \cdot H_2O$.[6] It seems reasonable to conclude that several different compounds are formed under various conditions, and that these are probably best regarded as tungsten tungstates, quite analogous to molybdenum blue. From this point of view W_2O_5 may be considered as $WO_2 \cdot WO_3$; W_3O_8 as $WO_2 \cdot 2\ WO_3$; W_4O_{11} as $WO_2 \cdot 3\ WO_3$; and W_5O_{14} as $WO_2 . 4\ WO_3$.

Tungstic acid,[7] H_2WO_4, is obtained as a yellow precipitate when a tungstate is treated with an excess of hot mineral acid. If a solution of a tungstate is acidified in the cold, the hydrated acid, $H_2WO_4 \cdot H_2O$, appears as a white, bulky precipitate, which is somewhat soluble in water, but readily changed to the insoluble H_2WO_4 on boiling. Most of the alkali tungstates

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[1] Van Liempt, *Zeit. anorg. Chem.* **119** 310 (1921).

[2] X-ray studies of WO_3 and its hydrates show that WO_3 is a different individual from H_2WO_4. *Zeit. anorg. Chem.* **121** 240 (1922).

[3] Malaguti, *Ann. chim. phys.* (2) **60** 271 (1835).

[4] Riche, *ibid.* (3) **50** 5 (1857); Desi, *J. Am. Chem. Soc.* **19** 213 (1897).

[5] v. Uslar, *Ann. Chem.* **94** 255 (1855).

[6] Allen and Gottschalk, *Am. Chem. Jour.* **27** 328 (1902).

[7] See "Acids of Tungsten," G. F. Hüttig, *Z. angew. Chem.* **35** 391 (1922), and "Colloidal Tungstic Acid," Moser and Erlich, *Edel Erden u. Erze* **3** 49 (1922).

are soluble, but certain tungstates of potassium and ammonium are sparingly soluble. Tungstates of calcium, iron, manganese, lead, and copper are found in nature and may be prepared artificially by precipitation.

Sodium tungstate, Na_2WO_4, is formed by the fusion of one mol of Na_2CO_3 or two of NaOH with one mol of WO_3 or by the complete dehydration of the hydrate. It is a white salt which exists in several distinct crystalline forms. It is soluble in water, forming a bitter, alkaline solution from which $Na_2WO_4 \cdot 2\,H_2O$ crystallizes above 6° and $Na_2WO_4 \cdot 10\,H_2O$ below this temperature. The dihydrate is the usual sodium tungstate of commerce. An acid tungstate, $2\,Na_2O \cdot 3\,WO_3 \cdot 7\,H_2O$, is obtained from the water solution of the fused paratungstate. It is readily soluble in water, giving a solution with a strong alkaline reaction.

Ammonium tungstate, $(NH_4)_2WO_4$, is probably present when H_2WO_4 is dissolved in an excess of ammonia. When the solution is evaporated generally a paratungstate is deposited. Calcium tungstate, $CaWO_4$, forms an amorphous white powder which has been suggested[1] as a substitute for white lead. Barium tungstate may be used in printing on fabrics.[2] Most of the metals form the normal tungstate $M^{I}_2WO_4$, and these salts are generally known in several hydrates.

Metatungstic acid, $H_2W_4O_{13} \cdot 7\,H_2O$, is prepared by decomposing the barium salt with sulfuric acid or the lead salt with hydrogen sulfide. It forms small yellow crystals which are readily soluble in water; they form the anhydrous acid at 100° and the anhydride on ignition.

The metatungstates are made by boiling the ordinary tungstates with tungstic acid until a filtered portion gives no precipitate on acidification. Most of the metatungstates are soluble in water and are prepared by reaction between barium metatungstate and the sulfate of the required metal. Since metatungstic acid is soluble, the acidification of a solution of a metatungstate produces no precipitate, but on long boiling H_2WO_4 is formed. The metatungstates are also formed by electrolysis of a tungstate solution when the increased acidity around the anode produces[3] the metatungstate. These compounds have the formula $M^{I}_2O \cdot 4\,WO_3 \cdot x\,H_2O$. The amount of water varies, but it is essential to their stability. The salts crystallize well, those of colorless bases forming colorless transparent crystals; they are efflorescent and isomorphous with the double boro-, phospho-, and silicotungstates.[4] The metatungstates give solutions which are rather weakly acid, with a very bitter taste, and in the presence of alkalies they revert to the normal tungstates. They are not precipitated by acids in the cold, but the normal acid is precipitated on long boiling. The metatungstates are distinguished from all other tungstate solutions by the fact that they are not precipitated by alkaline earth or other heavy metal cations except mercurous and lead salts. Ether precipitates metatungstic acid almost completely; alkaloids and other organic bases are precipitated in acid solution by metatungstates.

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[1] Schoen, *Jour. Soc. Chem. Ind.* **19** 740 (1900).

[2] Scheurer, *ibid.* **17** 921 (1898).

[3] Schaefer, *Z. anorg. Chem.* **38** 174 (1904).

[4] Copaux, *Ann. chim. phys.* (8) **17** 217 (1909).

Sodium metatungstate, $Na_2W_4O_{13} \cdot 10\,H_2O$, crystallizes from solution in shining tetragonal crystals which effloresce in dry air. Ammonium metatungstate forms both a hexa- and an octohydrate. The latter loses seven molecules of water at 100°, ammonia begins to come off at 120°, while the last molecule of water is not given up under 200°. The hexahydrate is precipitated by the addition of alcohol to the metatungstate solution. Barium metatungstate, $BaW_4O_{13} \cdot 9.5\,H_2O$, is prepared by mixing hot solutions of $Na_2W_4O_{13}$ and $BaCl_2$ containing a little HCl. On cooling, barium metatungstate crystallizes out, but it should be purified by recrystallization. The crystals are stable in the air, but at 100° they give up six molecules of water, the remainder passing off gradually up to 220°, when decomposition begins. Barium metatungstate is used commonly in the preparation of other metatungstates.

Paratungstic acid is possibly present when dilute solutions of barium paratungstate and sulfuric acid are mixed,[1] but attempts to concentrate the acid produce tungstic acid.

Paratungstates are among the most important of the tungstates, yet their composition is uncertain. Marignac concluded that most of the paratungstates were to be represented by the formula $5\,R_2O \cdot 12\,WO_3 \cdot x\,H_2O$; but a few were probably better represented by $3\,R_2O \cdot 7\,WO_3 \cdot x\,H_2O$. It is not impossible to conclude that these compounds are solid solutions of ordinary compounds. They are always hydrates which are completely dehydrated at temperatures at which they are decomposed into normal salts and insoluble tetratungstates. The alkali paratungstates are somewhat less soluble than the corresponding normal salts, but the solubility of the other paratungstates is similar to the normal salts.

Sodium paratungstate[2] may be prepared by saturating a solution of Na_2CO_3 or NaOH with WO_3; by nearly neutralizing a boiling solution of Na_2WO_4 with HCl; or by adding sodium metatungstate to a solution of the normal tungstate. The potassium salt is made in a similar manner.

Ammonium paratungstate is the usual salt which crystallizes from a solution of the hydrates of WO_3 in an excess of ammonia. It may be either $5(NH_4)_2O \cdot 12\,WO_3 \cdot 11\,H_2O$ or $3(NH_4)_2O \cdot 7\,WO_3 \cdot 6\,H_2O$, if crystallization takes place at ordinary temperatures. There are two crystal forms, needles and plates, both of which are stable in the air but lose most of their water at 100°. At 15°–18° it is soluble in 22 parts of water (Marignac), but the solubility is easily increased, possibly by a transformation of the salt or by loss of ammonia. On boiling the solution ammonia escapes and the salt goes slowly but completely over to the metatungstate. The dry salt begins to lose ammonia at 60° and on ignition there remains either the blue oxide or, in an excess of air, WO_3. Ammonium paratungstate is of great importance in the purification of tungsten material.

Tungsten bronzes are compounds obtained by the reduction of tungstates of the alkali and alkaline earth metals. The composition of this series of compounds corresponds in general to the formula $R_2O \cdot (WO_3)_x \cdot WO_2$,

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[1] L. A. Hallopeau, *Compt. rend.* **121** 61 (1895).

[2] See Edgar F. Smith, *J. Am. Chem. Soc.* **44** 2027 (1922).

in which x may vary from one to seven. They are intensively colored and extremely resistant to both acid and alkaline reagents; they are attacked only by hot concentrated aqua regia or fusion with such reagents as the alkalies, sulfur, ammonium persulfate, or ammonium acid sulfate. They may be prepared by reduction at high temperature of the acid tungstates with hydrogen, illuminating gas, or metallic tin; by the electrolytic reduction of the fused polytungstates; or by the fusion of a normal tungstate with WO_2 in the absence of air. Lithium-tungsten bronzes vary from steel-blue to violet; the sodium and potassium bronzes are golden yellow, purple red, violet, or blue; strontium gives red, carmine, or violet, while the barium compounds are dark red, yellowish-red, or violet. These materials are used as substitutes for bronze powders.

Complex tungstic acids are numerous and interesting. Phosphoric, arsenic, antimonic, vanadic, and boric acids condense with varying amounts of tungstic acid. The ratio of the other oxide to WO_3 varies from 1 : 7 to 1 : 24 or more.

Phosphotungstic acid, $H_3PO_4 \cdot 12\ WO_3 \cdot x\ H_2O$, is obtained as heavy greenish crystals when a solution containing the correct proportion of orthophosphoric and metatungstic acids is evaporated; or it may be prepared by adding sulfuric acid to a concentrated solution of sodium phosphate and sodium tungstate and extracting the phosphotungstic acid with ether. This acid is commonly used for precipitating alkaloids, proteins, and potassium and ammonium ions.

Silicotungstic acid,[1] $4\ H_2O \cdot SiO_2 \cdot 12\ WO_3 \cdot 22\ H_2O$, forms yellowish-white rhombic crystals which are readily soluble in water, alcohol, and ether. Mercurous silicotungstate is insoluble in water, but most of the other salts are soluble. Silicotungstic acid is used as a mordant for basic aniline dyes, and it is an excellent reagent for alkaloids.

Borotungstic acids containing one mol B_2O_3 in combination with 9, 24, or 28 mols WO_3 are described.[2] The mono-acid is a yellowish liquid of specific gravity about 3.0. The salts of these acids are comparable to the silicotungstates, but they are less easily crystallized and less stable. Cadmium borotungstate of approximately the formula $2\ CdO \cdot B_2O_3 \cdot 9\ WO_3 \cdot 18\ H_2O$ melts in its own water of crystallization at about 75°, giving a very dense yellow liquid in which minerals of a density up to 3.55 float. It is used for separating minerals of different densities.

In addition to the compounds in which two acids are represented, others have been described in which triple[3] complex acids are present; salts containing four or five acid radicals are also described.[4] The molecules of such compounds must be enormously complex, as is shown by the tentative formula for ammonium phospho-arseno-vanadio-vanadico-tungstate,

$$99(NH_4)_2O \cdot 12\ P_2O_5 \cdot 2\ As_2O_5 \cdot 66\ V_2O_5 \cdot 6\ V_2O_3 \cdot 191\ WO_3 \cdot 522\ H_2O.$$

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[1] See the work of Marignac; also Wyrouboff, *Bull. soc. franc. Min.* **19** 219 (1896); Rosenheim and Jaenicke, *Z. anorg. allgem. Chem.* **101** 235 (1917).

[2] H. Copaux, *Ann. chim. phys.* **17** (8) 217 (1909); *Compt. rend.* **147** 973 (1909); Rosenheim, *Z. anorg. Chem.* **70** 418 (1911).

[3] Smith and Exner, *J. Am. Chem. Soc.* **24** 573 (1902).

[4] Allen Rogers, *ibid.* **25** 298 (1903).

Pertungstic acid and its derivatives are little known compounds formed by the action of hydrogen peroxide on tungstic acid or the tungstates, usually at the boiling temperature. They are easily soluble, unstable, and difficult to purify. The valence of tungsten in these compounds appears to be higher than six.

Fluorine forms the interesting compound WF_6. It may be prepared by the action of HF or AsF_3 on WCl_6 in a platinum retort; or by interaction of SbF_5 and WCl_6 in glass. The tungsten hexafluoride is distilled out at about 90° and condensed in a thoroughly cooled flask. It is a liquid with a slight yellow color; it boils at 19.5° and solidifies at 2.5°, forming a white mass. Under ordinary conditions it is a gas, about ten times as heavy as air. It is completely hydrolyzed by water, but the dry gas attacks glass only slightly. Oxyfluorides are known.

Chlorine gives four chlorides and several oxychlorides. The dichloride, WCl_2, is a gray powder prepared by reduction of WCl_6 in hydrogen or by heating the tetrachloride in CO_2. It is quickly changed in air, and in contact with water a part is dissolved, but the greater part is changed to brown WO_2, HCl being liberated. The tetrachloride, WCl_4, is made by reducing either of the higher chlorides. It is a brownish powder, crystalline, nonvolatile, and hygroscopic. It is partly decomposed by cold water, yielding the brown oxide and HCl. The pentachloride, WCl_5, is obtained by gentle reduction of WCl_6 with hydrogen. It forms black or dark green crystals, which are easily volatile and extremely hygroscopic; some dissolve in water, but a greater part are hydrolyzed, yielding the blue oxide and HCl.

Tungsten hexachloride, WCl_6, is prepared by burning the metal in pure, dry chlorine. If moisture or oxygen is present, the red oxychloride is formed, and this is very difficult to remove. The hexachloride forms dark violet crystals, which when pure are stable in air and cold water. But in the presence of the oxychloride it absorbs moisture from the air and decomposes in cold water. This compound has been used[1] in some of the most accurate determinations of the atomic weight of tungsten.

Two oxychlorides are of interest. WO_2Cl_2 is prepared by passing chlorine over hot WO_2. It forms crystals which are stable in moist air and are only partly decomposed by boiling water. Tungsten oxytetrachloride, $WOCl_4$, is obtained by passing WCl_6 vapor over hot oxide or dioxydichloride. It forms red needles, which are quickly changed in air, forming a crust of tungstic acid.

Bromine forms WBr_2, WBr_5, WBr_6, $WOBr_4$, and WO_2Br_2. *Iodine* forms WI_2 and WI_4. All of these compounds are similar to the corresponding chlorine derivatives.

Sulfur combines directly with hot tungsten, forming WS_2. This compound may also be formed by the action of H_2S on the heated metal or WCl_6. It forms a soft, dark gray powder or small, black, friable crystals. It is insoluble in water, burns in the air, forming WO_3, but when heated in the absence of air, sulfur is expelled, leaving the metal.

Tungsten trisulfide, WS_3, when prepared by heating WS_2 in sulfur vapor, is a chocolate-brown powder which burns in air, combines easily with chlor-

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[1] Smith and Exner, *Proc. Am. Phil. Soc.* **43** 123 (1904)

ine, but is not completely reduced by hydrogen.[1] It forms colloidal solutions and dissolves in alkali hydroxides, carbonates, and sulfides, forming dark brown solutions which contain sulfo- and oxy-sulfotungstates. The trisulfide is prepared in the wet way by dissolving WO_3 in ammonium sulfide and acidifying; or by adding acid to a solution of an alkali tungstate which has been saturated with H_2S.

Sulfotungstates of the alkali and alkaline earth metals are formed when tungstates are saturated with H_2S or when hydrated tungstic oxide is dissolved in hydrosulfide. They vary in color from pale yellow to yellowish brown, and in general they crystallize well. When the alkalinity of the solutions is decreased, WS_3 is precipitated. Potassium sulfotungstate, K_2WS_4, forms yellow rhombic crystals, which melt without decomposition and dissolve readily in water. On standing in the air WS_3 and S precipitate.

Ammonium sulfotungstate, $(NH_4)_2WS_4$, is made by dissolving $H_2WO_4 \cdot H_2O$ in an excess of ammonia and saturating the solution with H_2S. It crystallizes in bright orange-colored crystals, which have a metallic iridescence and are stable in dry air but not in the presence of moisture. When heated, a residue of WS_2 is obtained. The crystals dissolve readily in water, forming a solution which slowly decomposes in the air. The formation of ammonium sulfotungstate makes it possible to separate tungsten from such elements as columbium by direct treatment of the ores.

Sulfotungstates of the alkaline earth metals are obtained by saturating the suspended tungstates with H_2S. On standing, the sulfosalts crystallize out.

Nitrogen does not react with metallic tungsten, but when the metal is heated in ammonia, a nitride is formed.[2] In the nitrogen filled tungsten lamp some WN_2 is formed,[3] but the reaction is probably between tungsten vapor and nitrogen. The compound collects as a brown deposit, which is stable in a vacuum at 400°, but is somewhat decomposed at 2200°. The compound W_2N_3 is formed by the action of ammonia on cold tungsten oxytetrachloride or hexachloride.[4]

Phosphorus combines directly with tungsten when its vapor is passed over the heated powder, forming a dark green compound of the formula W_3P_4. WP_2 is prepared by heating WCl_6 in dry PH_3; this compound forms black crystals which are stable in the air, which melt without decomposition, and which are insoluble in water and organic solvents. The compound WP is made by heating WP_2 with copper phosphide; and W_2P by reduction of a mixture of phosphoric and tungstic acids.

Arsenic forms the compound WAs_2, which is like the corresponding phosphide.

Carbon combines with tungsten, giving compounds whose composition appears to vary under different circumstances. Heating powdered tungsten with gases containing carbon readily yields[5] WC at 860° and W_3C_4 at 1000°.

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[1] Weiss, Martin, and Stimmelmayr, *A. anorg. Chem.* **65** 279 (1910).

[2] Henderson and Galletly, *Jour. Soc. Chem. Ind.* **27** 387 (1908).

[3] Langmuir, *Jour. Am. Chem. Soc.* **35** 931 (1913).

[4] Rideal, *ibid.* **55** 41 (1889).

[5] Hilpert and Ornstein, *Ber.* **46** 1669 (1913).

Heating tungsten oxide with carbon or calcium carbide produces[1] a compound of the formula W_2C or WC, depending[2] on the amount of iron present. Compounds of the formulae W_3C and W_3C_2 are also mentioned. It is possible that these so-called compounds represent solid solutions of carbon and tungsten.[3]

Detection. — Tungsten in its ores is usually detected by extraction and test of the soluble tungstate as follows: —

(*a*) If HCl is added to a tungstate solution at room temperature, a flocculent white precipitate of the hydrated tungstic acid appears; on boiling, the precipitate turns yellow, due to formation of H_2WO_4. Both precipitates are readily soluble in ammonia and the alkalies, but highly insoluble in acids. The presence of phosphoric, arsenic, boric, tartaric, or oxalic acids interferes with the precipitation. A columbate also produces a white precipitate on acidification, but this precipitate is distinguished by its greater solubility in water and hydrofluoric and hot concentrated sulfuric acids.

(*b*) When zinc or, better, tin[4] is added to tungstic acid suspended in a mineral acid, reduction takes place, giving the tungsten blue precipitate. In the presence of phosphoric acid a blue-colored solution is formed. Similar colors may be produced by molybdenum, columbium,[5] vanadium, and titanium; molybdenum gives a black as the final reduction product; the columbium blue is less intense and disappears on dilution; vanadium blue is produced by tartaric acid, which does not reduce tungsten; and the titanium color has a marked violet tint.

(*c*) Tungsten in steel may be detected by the fact that on solution of the steel in sulfuric acid the tungsten remains as a black residue which turns yellow on adding HNO_3.

(*d*) WO_3 and MoO_3 may be separated by the fact that if the dried mixture is extracted with selenium oxychloride, the latter dissolves while the former does not.

(*e*) A soluble tungstate may be detected by dipping a strip of filter paper into the solution, then moistening the strip with HCl and warming; the yellow WO_3 appears. If the paper is moistened with $SnCl_2$ solution and warmed, the blue of the lower oxides develops.

(*f*) A solution of cinchonine or quinine is said to precipitate WO_3 quantitatively.[6]

(*g*) The presence of 0.1 of a milligram of tungsten may be detected, even in mixture with molybdenum, by the microchemical identification of the characteristic crystals of ammonium paratungstate.[7]

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[1] Moissan, *Compt. rend.* **123** 13 (1896); **125** 839 (1897).

[2] Williams, *ibid.* **126** 1722 (1898).

[3] See diagram of W-C system, Ruff and Wunsch, *Z. anorg. Chem.* **85** 292 (1914).

[4] Zinc reduces tungsten so rapidly that the blue color may be overlooked in the presence of a small quantity of tungsten. The action of tin is slower.

[5] The color produced by columbium becomes brown.

[6] *Chem. Trade Jour.* **64** 298 (1919); also *Bull. Inst. Min. and Met.* 164 (1918). For other tests see Torossian, *Am. Jour. Sci.* **38** 537 (1914); Hartmann, *Chem. News*, **114** 45 (1916); *Atti accad. Lincei*, **28** I, 390 (1919).

[7] Van Liempt, *Z. anorg. allgem. Chem.* **122** 336 (1922).

Estimation.[1] — A fairly accurate measure of the amount of tungsten in an ore may be made by a simple specific gravity determination, the per cent WO_3 being read from tables. This method gives satisfactory results on any one ore, provided the gangue is quite uniform and other heavy minerals are absent. It is not reliable, however, since it permits the "salting" of an ore with barite, cassiterite, etc.

Quantitative methods are numerous, but many fail to give concordant results, especially under varying conditions. Usually the tungsten is weighed as WO_3, which may be obtained (*a*) by ignition of ammonium tungstate; (*b*) by ignition of mercury tungstate; (c) by decomposing alkali tungstates in the presence of HNO_3, the mixture being evaporated to dryness and extracted with water, then the insoluble WO_3 being filtered out, dried, and weighed; or (*d*) by precipitating lead tungstate and boiling with strong HCl. The insoluble tungstic acid is separated.

A colorometric method for determining tungsten has been devised,[2] depending on the reduction of the tungstic acid to the blue oxide. The solution of sodium tungstate is carefully acidified with standard HCl, care being taken to avoid a greater acidity than 10 cc. of normal acid per 100 cc. of solution. Then a slight excess of titanous chloride is added and the color compared with that obtained from a standard sodium tungstate solution. The colloidal suspension cannot be relied on to last longer than about 30 seconds, and vanadium, phosphorus, and molybdenum interfere.

Volumetric methods are not as reliable as the gravimetric and are mainly serviceable for comparative purposes. In one method, WO_3 is dissolved in excess of standard sodium hydroxide, and the excess titrated; a similar method uses ethylamine to dissolve the WO_3, the excess being then titrated with oxalic acid. Silica, tantalum, and columbium do not interfere with the latter method. An attempt to reduce tungsten to the blue oxide, then titrate back with ferric alum in the presence of thiocyanate, has not been successful.[3] Somewhat more accurate results are obtained by precipitating a neutral solution of ammonium tungstate with an excess of lead acetate and titrating the excess lead by means of ammonium molybdate.[4]

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[1] For detailed information see Schoeller and Powell, *Analysis of Minerals and Ores of the Rarer Elements*, pp. 174–182. *Anales soc. quinn Argentina*, **5** 81 (1917); *Eng. Min. Jour.* **105** 308 and 836 (1918); *Jour. Soc. Chem. Ind.* Dec. 16 (1918), p. 732 A; *ibid.* **37** 609 A (1919); *Min. and Sci. Press*, **118** 432 (1919).

[2] Travers, *Compt. rend.* **166** 416 (1918).

[3] Knecht and Hibbert, *Proc. Chem. Soc.* (1909) 277.

[4] Gastone Fiorentino, *Giorn. chim. ind. applicata*, **3** 56 (1921). *C. A.* **15** 3048 (1921).

CHAPTER XVI

GROUP VI — URANIUM

Historical. — The mineral pitchblende has been known for a long time, but its composition was a matter of dispute. By some it was considered an iron ore, others considered zinc its main component, while still others thought its great weight indicated that it must be an ore of the newly discovered element, tungsten. In 1789 Klaproth called attention to the fact that the ore contained what he called "a half metallic substance" which differed unmistakably from iron, zinc, and tungsten. By reduction of the yellow calx he obtained a metallic appearing substance which he supposed was a new metal. He suggested the name uranium in honor of the planet Uranus, which had been discovered by Herschel in 1781. Richter, Arfvedson, and Berzelius worked with similar materials and considered Klaproth's reduction product as the element. It was not until 1841 that Peligot discovered that the substance was really a lower oxide of uranium and in the following year he produced the metal itself and determined its equivalent.

Uranium and all its compounds are radioactive. The discovery of this fact in 1896 by Henri Becquerel[1] is of great historic interest since uranium was the first element which was found to possess the property of radioactivity. Following this interesting discovery, a search was made for other naturally radioactive substances, and in 1898 Schmidt announced[2] that all substances containing thorium, either in elementary form or in combination, gave off a similar radiation and somewhat later Rutherford discovered that thorium produced also a highly radioactive gas which he called the emanation. These early discoveries were rapidly followed by others upon which our knowledge of radioactivity is based.

Occurrence. — Uranium is not a common element, but it is found in a number of minerals,[3] most of which are rare. All uranium ores are radioactive, and the amount of uranium is an accurate index of the radium content,[4] since it is found that one part of radium is naturally in equilibrium with 3.2×10^6 parts of uranium; or, in other words, an amount of ore which contains a ton of the element uranium will be found to contain 320 milligrams of the element radium.

The most important uranium ores are pitchblende or uraninite

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[1] *Compt. rend.* **122** 501, 689, 762 (1896).

[2] Wied. *Ann.* **65** 141 (1898).

[3] For a list of uranium minerals see U. S. Bur. Mines *Bull.* 70.

[4] See U. S. Bur. Mines *Tech. Paper* 88.

and carnotite. The latter is described under radium. The former is essentially U_3O_8, which may be considered uranium uranate, $UO_2 \cdot 2\,UO_3$ or $U^{IV}(U^{VI}O_4)_2$, although in its natural form the substance contains widely varying proportions of quadrivalent and hexavalent uranium. The ore contains 75–90 per cent U_3O_8, the remainder being compounds of thorium, the rare earth metals, and lead, calcium, iron, arsenic, and bismuth, along with silica and water; radium is always present and gases such as nitrogen, helium, and argon sometimes make up as much as 2.6 per cent. The mineral is generally green or black in color with a pitchy luster, from which fact the name pitchblende is derived. It is found in Bohemia, Saxony, Hungary, Norway, Cornwall, East Africa, India, Australia, Madagascar, Ontario, Connecticut, the Carolinas, Texas, South Dakota, Colorado, and Wyoming.[1]

Uranium is commonly associated with thorium and the rare earths, generally in the form of tantalates, columbates, titanates, phosphates, arsenates, and vanadates. In addition to these, uranium is found in many rare minerals, such as autunite, sometimes called uranium mica, calcium uranyl phosphate; torbernite copper uranyl phosphate; the rare earth ores, fergusonite, samarskite, euxenite, and xenotime. A new mineral, brannerite, is reported[2] to contain more uranium than any other complex mineral except pitchblende. It is a complex uranium titanate, containing thorium and the rare earth elements along with small amounts of silicon, iron, calcium, strontium, barium, zirconium, and lead. Asphaltite bearing 1.13 to 2.88 per cent uranium has been found in Utah.[3]

The oldest and most celebrated deposits of uranium ores are the pitchblendes at Joachimsthal, Austria, whose mines have been worked since 1517. But only since about 1905 has uranium been sought, and for some time these deposits furnished the world's most important supply of uranium and radium. Since the development of the carnotite industry of Colorado, however, the United States has been the leading producer of both.

The production of uranium ores has varied widely, and the price has shown similar fluctuations. The price is sometimes

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[1] "New Deposit," *Science*, **49** 441 (1919).
[2] *Jour. Frank. Inst.* **189** 225.
[3] F. L. Hess, *Eng. Min. Jour. Press*, **114** 272 (1922).

determined by the radium content alone, though usually the amount of U_3O_8 is the determining factor and occasionally allowance is also made for the vanadium content of the ore. During 1919 carnotite containing a minimum of 2 per cent U_3O_8 sold for $2.75–$3.00 per pound of contained U_3O_8. In 1920 the price of similar ore was $2.25 per pound U_3O_8; in January, 1922, carnotite is quoted at $1.25–$1.75 per pound of U_3O_8.

Extraction. — The extraction of uranium from its ores is accomplished by a great variety of methods, the process selected depending on the nature of the ore, and the desirability of recovering other substances along with the uranium. It is important to notice that radium is the most valuable constituent of all uranium ores, consequently, the treatment will be such as to extract the largest possible proportion of radium. From this point of view uranium is always a by-product whose extraction is of secondary interest.

For the extraction of uranium from carnotite see the discussion of the extraction of radium (p. 60) and especially of vanadium (pp. 207–208, including Figure 13).

The extraction of uranium from pitchblende[1] presents some complications because the mineral fuses with difficulty, and extraction with acid is tedious, expensive, and incomplete. At Joachimsthal no less than seven methods have been tried out, the last one being roasting with lime in an oxidizing atmosphere. The desired reaction is: $2\,U_3O_8 + 6\,CaO + O_2 = 6\,CaUO_4$. At the same time vanadium, tungsten, and molybdenum are transformed into calcium salts, which are extracted with the uranium when the melt is ground and lixiviated with dilute sulfuric acid. These soluble salts are filtered out, ferric chloride is added, and the solution neutralized with Na_2CO_3, when ferric vanadate is precipitated. The solution containing the uranium is evaporated to dryness and the uranium dissolved in dilute alcohol, and from the alcoholic solution it is precipitated as ammonium uranate by the addition of ammonia. After filtering and washing with water containing NH_4Cl, the ammonium uranate is dried and sold as "lemon-yellow uranium." Its uses are similar to those of sodium uranate.

Uranium usually comes onto the market as sodium diuranate, $Na_2U_2O_7 \cdot 6\,H_2O$, which is known in the trade as the "yellow

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[1] See G. Gin, *Trans. Am. Electrochem. Soc.* **35** 191 (1919).

oxide of uranium." It may be prepared by roasting pitchblende with Na_2CO_3 and extracting the melt with dilute sulfuric acid when the soluble uranyl sulfate is formed. Sodium diuranate is precipitated by adding NaOH, or by neutralizing the solution and boiling vigorously. After the precipitate is pressed and dried it is ready for the market. The substance sold as uranium oxide is usually U_3O_8, which is prepared by precipitating ammonium uranate from the sulfuric acid solution. If this substance is digested with ammonium carbonate and ammonium hydroxide and then allowed to cool, crystals of ammonium uranyl carbonate are formed, and these on ignition yield U_3O_8. There is, also, sold some of the black oxide of uranium, which is UO_2 and some uranium salts like the nitrate, acetate, or sulfate.[1] Quite recently ferrouranium has become an important article of commerce.

Separation.[2] — Uranium may be separated from copper, bismuth, arsenic, etc., by the fact that it is not precipitated from acid solution by H_2S. The separation from lead is best accomplished by adding sulfuric acid to the nitrate solution and evaporating to fumes.

The rare earths are removed by adding oxalic acid to a hot solution and filtering off the rare earth oxalates. To decompose the excess oxalic acid in the filtrate, evaporate to dryness, ignite, and take up the residue with HCl. If necessary any insoluble residue may be brought into solution by fusion with $KHSO_4$.

Uranium is separated from other metals of the third group by the fact of its solubility in solutions of alkali carbonate. Separation is accomplished by adding to a solution containing uranium an excess of ammonia, ammonium carbonate, and ammonium sulfide. The uranium remains in solution while such metals as iron, cobalt, manganese, zinc, and titanium are precipitated. From the filtrate the uranium may be precipitated by removing the H_2S completely and adding ammonia. This treatment does not give complete separation from nickel, aluminium or beryllium. Nickel may be removed by long boiling of a dilute solution containing Na_2CO_3. Aluminium is sepa-

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[1] For method of preparation see Parsons, *Jour. Ind. and Eng. Chem.* **9** 466 (1917); also, R. J. Anderson, *Trans. Am. Electrochem. Soc.* **37** 281 (1920).

[2] See Kern, *Jour. Am. Chem. Soc.* **23** 685 (1901); Brearley, *Analytical Chemistry of Uranium*, London, 1903; and Pierle, *Jour. Ind. and Eng. Chem.* **12** 60 (1920).

rated[1] by precipitating the phosphates, boiling first with nitric acid, then with sodium carbonate. Zirconium is precipitated as a phosphate in the presence of $H_2O_2 + H_2SO_4$. Vanadium is precipitated as lead vanadate by adding lead acetate and ammonium acetate to a solution containing a slight excess of nitric acid.[2]

Metallurgy. — Uranium may be prepared by several methods: (*a*) reduction of UCl_4 with sodium[3] or potassium; (*b*) reduction of U_3O_8 with charcoal in an electric furnace;[4] to free the product from carbon it is heated with U_3O_8 in the presence of titanium, which is used to prevent nitrogen from combining with uranium; (*c*) reduction of UO_2 or UO_3 has been accomplished by means of aluminium;[5] UO_3 has also been reduced by calcium;[6] (*d*) reduction by means of calcium carbide either with or without a mixture of ferrosilicon has been effected,[7] although the Bureau of Mines finds that coke at the temperature of the electric arc is more effective than either; (*e*) electrolysis of fused sodium-uranium chloride in an atmosphere of hydrogen.[8] Use of a current of 50 amperes at 8–10 volts keeps the bath fluid, and the metal contains about 0.5 per cent impurities.

Properties. — Pure uranium is white, but the metal frequently has a yellow color due to the presence of some nitride. The metal prepared by electrolysis is deposited as small shining crystals; other methods of preparation give either a black powder or a white compact mass. The metal takes a polish well, is somewhat malleable, is softer than steel, and when heated with carbon and chilled it becomes very hard and brittle. Probably the most accurate melting point determination[9] gives a value of 1850°; the specific gravity is 18.685 at 13°; the specific heat at 0° is 0.0276; it is slightly paramagnetic, the magnetic susceptibility being $+ 0.21 \times 10^{-6}$.

The powdered metal burns in oxygen at 170°, in fluorine at room temperature, in chlorine at 150°, in bromine at 210°, in

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[1] Brearley, p. 185.

[2] U. S. Bur. of Mines, *Bull.* 70.

[3] R. W. Moore, New York meeting Am. Electrochem. Soc. May, 1923.

[4] Moissan, *Compt. rend.* **116** 347 (1893).

[5] Aloy, *Ann. chim. phys.* (7) **24** 412 (1901); Stavenhagen, *Ber.* **32** 3065 (1899).

[6] Burger, *Diss. Basel*, 1907, p. 19; Kuzel and Wedekind, French Pat. Oct. 17, 1910.

[7] German Pat. June 11, 1912.

[8] Moissan, *Compt. rend.* **122** 1088 (1896).

[9] Guertler and Pirani, *Zeit. für Metallkunde*, **11** 1 (191).

iodine at 260°, in sulfur vapor at 500°, and in nitrogen at 1000°. It decomposes water slowly at ordinary temperatures and more rapidly at the boiling temperature. Dry hydrogen chloride gas attacks the metal at a dull red temperature, and at a slightly higher temperature it reacts with ammonia liberating hydrogen and forming a dark crystalline powder. It dissolves in dilute HCl and H_2SO_4, liberating hydrogen and forming quadrivalent salts, while with concentrated sulfuric acid SO_2 is evolved. The powdered metal dissolves readily in nitric acid, liberating the oxides of nitrogen, but the fused metal reacts only slowly with nitric acid even when warm. The caustic alkalies apparently have no action upon it. Uranium will displace mercury, silver, copper, and tin from the solutions of their salts. The exact position of uranium in the electromotive series has not been determined because of lack of pure uranium, but an alloy containing 8.34 per cent of iron gave -0.093 volt.[1]

In addition to the property of radioactivity, the salts of uranium possess peculiar properties with respect to light. When a solution of a uranium salt is exposed to light it seems to absorb energy which is later given off in the form of fluorescence.[2] The presence of such substances as chlorine or iodine ions, ferric or vanadyl salts, vanadic acid or quadrivalent uranium compounds, inhibits the fluorescence. In accordance with the theory that the photosensitizing effects of such fluorescent compounds as eosin are due to simultaneous oxidation and reduction, fluorescence in uranium salts is explained by the fact that in the light the uranyl ions are partly reduced to the trivalent condition and partly oxidized to the octavalent condition. When these two forms react with each other in a reverse manner to produce the hexavalent form, fluorescence results. The effect of inhibiting substances is explained by the supposition that iodine, for example, unites directly with the trivalent uranium, giving at once the hexavalent form.

Uses. — Uranium finds few commercial applications, although several possible uses have been suggested. For a time an impure form of the metal containing some carbide was used as a sparking medium for automatic cigar lighters. These have now been superseded by cerium alloys, which are more highly pyro-

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[1] *Jour. Phys. Chem.* **23** 517 (1919).

[2] E. Bauer, "The Photolysis of Uranium Salts," *Chem. Ztg.* **2** 40 (1918).

phoric. Many attempts have been made to utilize uranium as an electrode in arc lamps, probably the most successful device being covered by a French patent which uses a mercury cathode and gives a powerful ultraviolet light, useful for sterilizing liquids. A plan for depositing uranium on a tungsten filament in an incandescent bulb has been patented.[1] The bulb is filled with nitrogen or argon and a little uranium chloride put in, then the bulb is exhausted, sealed, and heated to decompose the chloride.

In ceramics uranium compounds are used to give colored glazes, especially yellow and orange. The compounds employed are either sodium or ammonium uranate, which are commonly sold under the name " uranium yellow "; or, the yellow or green oxide. As little as 0.006 per cent gives a good yellow color, but on increasing the amount the color may be varied[2] to orange, brown, dark olive green, or black. A deeper shade of green is said to be given by U_3O_8 than can be produced by chromium compounds.[3] The amount of lead in the glaze also influences the color obtained. A bright vermilion glaze is made by mixing 57 parts of red lead, 20 parts feldspar, 2 parts zinc oxide, 12 parts of flint, and 9 parts of U_3O_8. As coloring materials in the manufacture of glass, they produce an opalescent yellow, which is green by reflected light. This type of glass is expensive since the amount of U_3O_8 used is sometimes as high as 20 per cent.

Uranium salts have been used as mordants for both silk and wool,[4] as well as in calico printing. Uranium salts also produce a pleasing brown dye on textiles when the fabric is first heated with solutions of uranium salts, and then the color is fixed by reduction with potassium ferrocyanide, gallic acid, or pyrogallol.

Metallic uranium and uranium carbide were found by Haber's investigation[5] to be among the best catalysts for the manufacture of ammonia by the direct union of the elements. The disadvantages in the use of these materials come from the cost and the ease with which the substances lose the ability to serve as a catalyst unless very pure hydrogen is used.

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[1] U. S. Pat. May 7, 1918; C. A. **12** 1617 (1918).

[2] *Trans. Am. Cer. Soc.* **8** 210 (1906); **9** 771 (1907).

[3] *Jour. Am. Cer. Soc.* **1** 238 (1918).

[4] *Farben Zeit.* **5** 17 (1894).

[5] Haber and Greenwood, *Zeit. Elektrochem.* **19** 53 (1913).

In photography many attempts have been made to utilize the salts of uranium. As early as 1864 a process was patented by Wothly for the use of a collodion solution of uranium nitrate and silver nitrate. This mixture was painted on to the surface of the paper, and after exposure under the negative, fixing was accomplished by immersion in dilute hydrochloric acid. The prints were toned with gold chloride. Pictures prepared by this process were known as Wothlytypes. This process seems to have been the immediate predecessor of the collodio-chloride papers, which are still used. In 1873 a dry collodion plate containing uranium salts appeared on the market. The present uses of uranium salts in photography seem to be limited to two purposes. Toning to a pleasing brown print is now accomplished by means of salts of uranium along with potassium ferrocyanide. The same chemical reaction is also used for the intensification of weak negatives. For the latter purpose, the negative is first carefully washed free from developing fluid, then soaked thoroughly in a solution of uranium nitrate or acetate, then washed, and finally immersed in a bath of potassium ferrocyanide, when the brown uranium ferrocyanide deepens the color of the image.

Uranium borate added to raw rubber in the refining process is said[1] to produce a product of improved appearance and increased tensile strength. Such rubber appears to resist oxidation more successfully than rubber not so treated.

In medicine the nitrate, salicylate, and chloride of uranium have been used as a remedy for gout, diabetes, and as a throat spray. The salts of uranium are active poisons,[2] interfering with the function of the haemoglobin and producing marked elevation of blood pressure as well as degeneration of the tissues of the blood vessels, nephritis, and violent inflammation of the intestines.

Uranyl nitrate has been used as a reagent for the rapid volumetric determination of phosphates or arsenates. The uranyl solution is standardized by use of a phosphate (or arsenate) solution of known strength. The end point both in standardizing and in titrating an unknown solution is determined by using a saturated solution of $K_4Fe(CN)_6$ as an outside indicator.

[1] *India Rubber World*, [illegible] 500 (1915).

[2] Jacob Woroschilsky, *Arbeiten d. Phar. Inst. Dorpat* V, 1890.

Uranium steels were apparently first prepared about 1897, when it was reported that the French government was experimenting upon the use of this alloy steel in ordnance. Various rumors have been afloat in regard to the use of uranium steel in Germany for armor plate and the linings of big guns; in England, Russia, and the United States in various special steels. The use of uranium in the steel industry must be regarded as in the early experimental stage, making its value and importance questions which the future alone can answer.

Ferrouranium[1] is the only form in which uranium is used in making steel because of the ease with which the element is oxidized, and the difficulty of obtaining a uniform mix. The production of a suitable ferrouranium is accompanied by some difficulties. The reduction with aluminium by the usual process is not successful since the product contains considerable aluminium, aluminium oxide, and uranium oxide. A special modification of the thermit process known as Stavenhagen's modification[2] gives better results. Attempts to prepare ferrouranium in the electric furnace have not been entirely successful, because the product obtained contains varying amounts of carbon, silicon, oxides, and usually vanadium. The indirect arc type of furnace required an excessive power consumption in order to get the required temperature.[3] Attempts to decarbonize the product by heating with iron oxide or uranium oxide were not successful, due to the excessive oxidation during the second heating. Best results were obtained by reducing UO_2 with a good grade of coke, using CaF_2 as a slag and a tilting direct arc type of furnace with water cooled magnesite hearth and sides. In this way a ferro-alloy containing 40–70 per cent uranium and less than 2.0 per cent carbon and 0.75 per cent silicon can be produced; by using a good grade of uranium material, the amount of vanadium may be kept below 0.5 per cent and aluminium, sulfur, phosphorus, and manganese may be kept so low as to be negligible. The ferrouranium made in the United States usually contains between 25 and 35 per cent uranium,[4] although

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[1] See R. M. Keeney, "Manufacture of Ferroalloys in the Electric Furnace," *Bull. A. I. M. E.* Aug. 1918, pp. 1321–1373; also, "Preparation of Ferro-Uranium," U. S. Bur. Mines, *Tech. Paper* 177 (1917).

[2] *Ber.* **35** 909 (1902).

[3] Gillett and Mack, *Jour. Ind. and Eng. Chem.* **9** 342 (1917); a temperature of at least 1700° C. is required for the reduction of UO_2 with carbon.

[4] See *Tariff Information Series*, C-1, "Ferro-alloy Industry" (1921).

by mistake the uranium content has been given as 35–50 per cent. The manufacture of this material in this country is carried on at a single plant, which is located at Canonsburg, Pennsylvania.

The addition of ferrouranium to steel is accompanied by heavy loss due to the oxidation of the uranium. This loss may be as high as $\frac{1}{3}$ to $\frac{1}{2}$ the uranium added. To reduce the loss as far as possible the ferrouranium is added just before or during pouring, and the temperature of the steel is kept low. If the ferrouranium contains more than 65 per cent uranium, oxidation is rapid, and if the amount is less than 40 per cent the uranium is not taken up well by the steel. Consequently, the favorite ferrouranium contains 40–65 per cent uranium. The best uranium steels are made in the electric furnace.

There are two rather striking effects produced by the addition of uranium to steel: (1) its beneficial results do not require intensification by the use of other alloys; (2) uranium increases the hardness of steel, so that such steels lend themselves readily to water quenching. The increased hardness is, however, not accompanied by an increase of brittleness to as great a degree as is induced by many other alloying substances. As a result carbon-uranium steels are especially serviceable for uses which require a low drawing temperature, since under these conditions they possess to a remarkable degree the combination of hardness, strength, and ductility.[1] Uranium is, however, frequently added to steel along with such other alloying elements as tungsten, molybdenum, vanadium, and chromium. Usually the amount of uranium is less than 1 per cent; high uranium steels have been studied very little. Over 3 per cent uranium is said to produce a product which cracks badly on forging. The general effect of uranium upon the properties of steel is similar to the influence of tungsten; consequently, the usual view is that the introduction of a small amount of uranium permits the saving of a considerable amount of tungsten. For example, the introduction of 3 per cent uranium, 8 per cent tungsten, and small amounts of chromium and vanadium produces a steel whose performance compares favorably with that of a steel which contains 18 per cent tungsten.

The properties claimed for uranium steels are as follows:[2]

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[1] Hugh S. Foote, "Uranium Steels," *Chem. and Met.* **25** 789 (1921).

[2] See also *ibid.* **15** 160 and 448 (1916); **22** 829 (1920); **25** 789 (1921).

increased hardness without decrease in ductility; increased elastic limit; greater tensile strength; and improved dynamic properties. Tools made of uranium steel are said to possess longer life because of the greater toughness and heat-resisting qualities. Shop tests made with uranium steel tools show that they possess cutting power, durability, and general efficiency on an average 20–50 per cent higher than that shown by tools made from the best grades of other high speed steels.[1] Enthusiastic claims are made that "the benefits obtained from the use of uranium certainly constitute the highest attainment of the steelmaker's art." However desirable the properties of uranium steel may prove to be, it seems likely that the future of this product will be determined largely by the relative cost of uranium and other alloying substances which produce similar effects upon steel. The question of a suitable ore supply is also a matter of great importance, especially with respect to uranium. But so long as uranium remains a by-product of the radium industry with sale for only a small part of the uranium produced,[2] the question of cost of raw materials should not be a serious one in the manufacture of uranium steel.

Compounds.[3] — Uranium forms several series of compounds which in general resemble the corresponding series of tungsten and molybdenum compounds. Uranium is, however, distinctly more basic in its tendency than any other member of this group. It appears frequently in the acid radical, forming both simple and polyuranates. Its greater basicity is shown by the fact that its trioxide forms a much smaller number of poly-derivatives than do molybdenum or tungsten. In most of its important compounds uranium acts as a metallic element. Uranium has valences of 2, 3, 4, 5, 6, and possibly 8, the compounds of valence 2 and 3 being relatively unimportant and formed by reduction of the higher compounds. In its valence of 4, uranium forms the important class of uranous compounds, which are usually prepared by reduction of the higher compounds. They resemble the ferrous compounds in the ease with which they are oxidized. In its hexavalent state uranium shows little tendency to form simple metallic salts, since UF_6 is the only compound of this

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[1] See "Comparative Test of High Speed Steels," *Chem. and Met.* **22** 829 (1920).

[2] S. C. Lind, U. S. Bur. of Mines, *Trans. Am. Electrochem. Soc.* **35** 197 (1919).

[3] E. Wilke-Dörfurt, "Preparation of Uranium Compounds in Pure State," *Wiss. Veroffent. Siemens-Konzern Soc.* **1** 143 (1920); C. A. **15** 2595 (1921).

TABLE XXXVII

Compounds of Uranium

VALENCE	OXIDE	HYDROXIDE	NATURE	TYPICAL SALTS	CHARACTERISTIC COLOR	CLASS NAME	REMARKS
U^{II}	UO	—	Basic	UF_2, US	—	Monosulfide	Obtained by reduction
U^{III}	U_2O_3	—	Basic	UCl_3, U_2S_3, $UH(SO_4)_2$	Red to brown	Trichloride	By reduction
U^{IV}	UO_2	$U(OH)_4$(?)	Basic	UCl_4, US_2 $U(SO_4)_2 \cdot x\,H_2O$	Blue to green	Uranous	Easily oxidized
U^{V}	U_2O_5	—	Basic	UCl_5, UBr_5	Red to brown	Pentachloride	
U^{VI}	UO_3	—	Feebly basic	UF_6	Light yellow	Hexafluoride	
		$UO_2(OH)_2 \cdot H_2O$	Basic	$UO_2(NO_3)_2$ UO_2SO_4	Yellow with green fluorescence	Uranyl	Most important
		$UO_4 \cdot H_2O$	Acidic	Na_2UO_4	Red to green	Uranates	Uranates are generally insoluble
				$Na_2U_2O_7$	Yellow	Di-uranates	
				$Na_2U_3O_{10}$	Golden	Tri-uranates	
				$Na_2U_5O_{16}$	Orange	Penta-uranates	
U^{VIII}	UO_4(?)	$UO_4 \cdot 4\,H_2O$	Acidic	$(Na_2O_2)_2UO_4 \cdot 8\,H_2O$	Yellow	Per-uranates	More stable than similar salts of Mo and W

sort known; but it readily forms uranates, both simple and complex. It also gives rise to the uranyl series of compounds, which are doubtless the most important of all the uranium salts. They may be regarded as derivatives of UO_3 which have been formed by replacing one oxygen with the equivalent amount of a negative element or radical. Thus, they always contain the bivalent radical UO_2, which is more markedly basic than the corresponding radicals of the other members of this group. Accordingly the uranyl compounds resemble more closely the salts of a basic oxide, while the corresponding derivatives of the other metals are like the acid chlorides, such as $POCl_3$ and SO_2Cl_2. This conception is strengthened by the fact that in water solution the uranyl salts of strong acids are slightly hydrolyzed, and under the influence of the electric current the uranyl ion concentrates around the cathode. The uranyl solutions have a yellow color with a strong greenish fluorescence, which is noticeable in uranium glass. These salts are particularly sensitive to light. Table XXXVII shows the relationship between the various classes of uranium compounds.

Oxygen forms the two definite oxides, UO_2 and UO_3, each of which is represented by one or more well defined series of compounds.

Uranium dioxide, UO_2, was for a long time considered as metallic uranium, because of its appearance and the fact that it is obtained by heating U_3O_8 in a stream of hydrogen. It is now prepared[1] on the large scale by reduction with carbonaceous material on fusion with sodium chloride, and used for the production of ferrouranium. When so prepared it is black in color from the excess carbon which it contains and is commonly called the black oxide of uranium. When obtained by reduction with hydrogen it is a brown or copper-colored powder, which is pyrophoric; it burns in air, oxidizing completely to U_3O_8. The uncalcined UO_2 dissolves in strong acids, forming the uranous series of salts; after ignition it is only slightly soluble in acids.

Uranous hydroxide is obtained as a bulky reddish-brown precipitate when alkalies are added to uranous solutions. The precipitate darkens on boiling and is easily oxidized by air in the presence of excess alkali, forming uranyl compounds. The formula for the compound is written either $UO_2 \cdot 2\,H_2O$ or $U(OH)_4$.

Uranium trioxide or uranic oxide, UO_3, may be prepared in pure form by long continued heating of uranyl-ammonium carbonate at 300° or of ammonium uranate at 250°; uranyl nitrate also yields UO_3 on ignition, but the product contains basic nitrates unless the heating is done thoroughly. The color of the oxide varies from orange to red, depending on the method

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[1] Robert J. Anderson, *Trans. Am. Electrochem. Soc.* **37** 281 (1920).

of heating. When ignited at higher temperatures it forms U_3O_8, and when heated with hydrogen it forms UO_2, or at 3000° it yields metallic uranium. It reacts readily with water at ordinary temperatures, forming H_2UO_4.

Uranic hydroxide is obtained as the monohydrate $UO_3 \cdot H_2O$ by the electrolysis of the nitrate or when the hydrated U_3O_8 is boiled with water in an open dish. A dihydrate, $UO_2(OH)_2H_2O$, is obtained by gently evaporating a solution of uranyl nitrate in absolute alcohol. The dihydrate loses half its water at 100° or when kept in a vacuum at ordinary temperature. These compounds react with alkalies to produce uranates and with acids to give uranyl compounds.

The uranates of the alkali metals are difficultly soluble and are prepared by precipitating uranyl solutions with an alkali. The uranates of the other metals may be made by adding ammonia to a mixture of a uranyl salt with the corresponding metallic salt. Generally the salt formed by precipitation is the di- or poly-uranate, $R'_2U_2O_7$. On fusion the monouranate R'_2UO_4 is generally obtained. Polyuranates containing as many as six molecules of UO_3 are known in combination with sodium and potassium, but the less positive metals form no compounds more complex than the diuranates. The most important uranate is sodium diuranate, $Na_2U_2O_7$, which is known commercially as uranium yellow. It is used in the manufacture of yellow uranium glass and as a pigment in coloring both glass and porcelain.

The green oxide of uranium, U_3O_8, is obtained by heating ammonium uranate or any oxide of uranium[1] in the air at 700°. The product prepared in this way has a definite composition and may be used as a basis for the quantitative estimation of uranium. If the ignition takes place at a lower temperature there is a tendency to form UO_3, which loses oxygen at 700°, forming U_3O_8; at higher temperatures or when heated in hydrogen, UO_2 is formed. After ignition the green oxide is difficultly soluble in mineral acids. It is the main component of the mineral uraninite or uranium pitchblende.

Chlorine unites with uranium, forming a trichloride, a tetrachloride, a pentachloride, and an oxychloride.

Uranium trichloride is obtained as a dark brown powder by the reduction of the tetrachloride with hydrogen which is free from oxygen; or by the action of zinc and hydrochloric acid upon uranyl salts. It is readily soluble in water, but reacts with it, quickly liberating hydrogen and forming a green solution.

Uranium tetrachloride or uranous chloride, UCl_4, is made by passing chlorine over a heated mixture of carbon and U_3O_8, by action of chlorine on uranium carbide, or by heating U_3O_8 to red heat in a stream of carbon tetrachloride. It forms beautiful dark green octahedral crystals which have a metallic luster and sublime at red heat. They are deliquescent, dissolve readily in water with marked evolution of heat, giving a solution which is strongly acid, due to hydrolysis. On boiling the solution liberates hydrochloric acid; it is a strong reducing agent.

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[1] McCoy and Ashman, Am. Jour. Sci. (4) 26 521 (1908).

Uranium pentachloride, UCl_5, is formed by adding chlorine to UCl_4. If the addition is made slowly, the pentachloride forms long needle-like crystals which have a dark green metallic luster by reflected light but a ruby red color by transmitted light. If the chlorine is added rapidly a brown crystalline powder is formed. Both forms are extremely hygroscopic and react vigorously with water, liberating HCl and $U(OH)_4$; it is soluble in many organic solvents.

Uranyl chloride, UO_2Cl_2, is formed by heating UO_2 to red heat in a stream of dry chlorine. It forms a yellow crystalline mass, which is hygroscopic and soluble in water. The water solution on slow evaporation forms a monohydrate. The anhydrous uranyl chloride is stable if it is kept away from moisture. The water solution has an acid reaction and upon heating liberates HCl. It forms double salts with the alkali chlorides, such as $2\ KCl \cdot UO_2Cl_2 \cdot 2\ H_2O$.

Sulfur forms a number of sulfides of uranium, of which the most important is the uranyl sulfide, UO_2S. This compound is thrown down as a dark brown precipitate when ammonium sulfide is added to a uranyl nitrate solution. It is soluble in ammonium carbonate and in acids and upon exposure to air it oxidizes quickly.

Uranous sulfate is not known in the anhydrous condition, but hydrates containing 2, 4, 8, and 9 molecules of water are easily prepared. Of these hydrates all except the dihydrate are isomorphous with corresponding hydrates of thorium sulfate. The octohydrate of uranous sulfate is the most common, it being formed by adding alcohol to a solution of U_3O_8 in dilute sulfuric acid.

Uranyl sulfate, $UO_2SO_4 \cdot 3\ H_2O$, is prepared by the crystallization of a solution of uranyl hydroxide in dilute sulfuric acid or by heating uranyl nitrate with sulfuric acid. It forms yellow-green crystals, which under the microscope show a beautiful fluorescence. On exposure to air they loose water slowly, and at 115° a monohydrate is formed while at 175° the anhydrous salt is produced. Both acid salts and double alkali sulfates are formed.

Nitrogen combines directly with uranium at a temperature of 1000°[1]; nitrogen or ammonia reacts with the carbide, yielding a nitride; dry ammonia also produces a nitride when it reacts with uranium tetrachloride. The formula of the nitride is usually U_3N_4. The catalytic influence of uranium carbide in the manufacture of ammonia by the Haber process is attributed[2] to the formation of the nitride.

Uranyl nitrate, $UO_2(NO_3)_2 \cdot 6\ H_2O$[3] is commonly called uranium nitrate and is the best known and most widely used uranyl salt. It may be prepared by dissolving any oxide of uranium in nitric acid. It forms lemon-yellow prisms which have a green fluorescence. They are readily soluble in water and are deliquescent. When shaken, rubbed, or crushed, the crystals show remarkable triboluminescence, with occasionally somewhat violent detonations. Numerous theories have been advanced to account

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[1] Moissan, *Compt. rend.* **122** 274 (1896).

[2] Haber and Greenwood, *Zeit. Elektrochem.* **21** 241 (1915); **19** 68 (1913).

[3] See also F. E. E. Germann, *Jour. Am. Chem. Soc.* **44** 1466 (1922).

for this peculiar behavior. It has been suggested that triboluminescence may be due to some peculiar property such as radioactivity of the uranium atom itself; or, that in crystallizing differences of electrical potential may be developed between crystals; or, that disturbances release some internal strain which has developed within the crystals. But the best explanation[1] of these phenomena seems to be based upon the partial replacement of water of crystallization by ether and an unstable lower oxide of nitrogen. This idea is strengthened by the observations that samples of uranyl nitrate which are strongly triboluminescent contain both ether and an oxide of nitrogen; that crystals of this salt do not display this property unless they have been prepared from an ether solution containing free nitric acid; and that such crystals loose their triboluminescence when recrystallized from water.

Carbon combines so readily with uranium that the reduction of the oxides with carbon always produces some carbide. Moissan prepared[2] the carbide by mixing 50 parts U_3O_8 with 8 parts charcoal and heating in the electric furnace. He assigned the formula U_2C_3 to the compound, but later work[3] makes the unusual formula UC_2 seem more probable. The compound has a metallic appearance, a crystalline fracture, and is strongly pyrophoric; it scratches glass and quartz but not corundum. It burns in oxygen at 370°, forming U_3O_8; it combines with fluorine at slightly elevated temperatures, forming UF_4 or UF_6. Chlorine attacks it at 350°, bromine at 390°, and iodine below red heat. In contact with water the carbide is decomposed, yielding hydrogen and a very complex mixture of gaseous, liquid, and solid hydrocarbons. Chief interest in the carbide is connected with its use as a catalyst in the Haber process.

Simple uranyl carbonates are not known, but double carbonates are easily formed; as, for example, a salt of the composition $UO_2CO_3 \cdot 2\,Na_2CO_3$ is obtained as a yellow crust, when freshly precipitated sodium uranate is treated with sodium bicarbonate, or when an excess of sodium carbonate is added to a solution of uranyl acetate.

Uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2\,H_2O$, is next to the nitrate the most important uranyl salt of commerce. It is prepared by the solution of uranyl hydroxide or oxide in acetic acid. It is soluble in water, forming a solution with a density of 2.89 from which it crystallizes in fluorescent prisms. It displays the phenomenon of photalysis.

Uranyl formates, oxalates, and tartrates are also formed.

Detection. — Uranium is precipitated in the Third Group and in the analysis undergoes numerous characteristic changes. (1) When present as a uranyl salt the addition of ammonia produces a precipitate of ammonium diuranate, $(NH_4)_2U_2O_7$, which appears as a yellow powder which is slowly transformed by ammonium sulfide to UO_2S, dark brown, soluble both in HCl and $(NH_4)_2CO_3$. (2) When NaOH is added to a solution of a uranyl

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[1] See Andrews, *Chem. Ztg.* **36** 423 (1912), Späth, *Wiener Monatsch.* **33** 853 (1912); Müller, *Chem. Ztg.* **40** 38 (1916), **41** 439 (1917); and J. A. Siemssen, *Chem. Ztg.* **46** 450 (1922).

[2] *Le Four electrique,* Paris, 1897; *Compt. rend.* **122** 274 (1896).

[3] Lebeau, *ibid.* **152** 955 (1911); *Bull. Soc. Chim.* (4) **9** 512 (1911).

salt, yellow $Na_2U_2O_7$ is precipitated; it does not dissolve in excess of alkali, but forms the deep yellow peruranate on addition of H_2O_2 or Na_2O_2. (3) When Na_2HPO_4 solution is added, uranium is precipitated as a gelat-nous yellowish-white precipitate of UO_2HPO_4, which is soluble in mineral acids but insoluble in acetic acid. In the presence of ammonium salts, vanadates do not interfere, but aluminium, beryllium, and lead must be absent. (4) The addition of $K_4Fe(CN)_6$ produces a red-brown precipitate of $(UO_2)_2Fe(CN)_6$, which dissolves in NaOH, HCl, or $(NH_4)_2CO_3$, forming yellow solutions. (5) Sodium salicylate produces a red coloration in a solution containing as little as 0.02 per cent uranium. Free acids, iron salts, alcohol, and acetone interfere. This reaction may be made quantitative by colorimetric methods. (6) When an excess of zinc is added to a nitric acid solution containing uranium, a yellow deposit collects on the zinc residue.[1]

Determination.[2] — Uranium may be determined quantitatively as U_3O_8, which may be obtained by precipitating a uranyl salt with $(NH_4)_2S$ and NH_4OH; or the U_3O_8 may be reduced to UO_2 by heating in a stream of hydrogen; or the addition of ammonium phosphate in the presence of ammonium salts and igniting to $(UO_2)_2P_2O_7$. Cupferron precipitates uranium quantitatively from aluminium, calcium, magnesium, and phosphorus; the precipitate is converted to U_3O_8 by ignition.[3]

Volumetrically uranium may be determined by reducing an acid solution with zinc or titanous sulfate and oxidizing to the uranyl state by permanganate according to such a reaction as: $2\,KMnO_4 + 5\,U(SO_4)_2 + 2\,H_2O = 2\,KHSO_4 + 2\,MnSO_4 + H_2SO_4 + 5\,UO_2SO_4$. A solution of uranyl acetate may be titrated with sodium phosphate. Titration with $\frac{N}{20}$ $K_2Cr_2O_7$ in the presence of an excess of sulfuric acid is recommended,[4] and electrometric titration is successful.[5]

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[1] Baur and Rebmann, *Helvetica Chim. Acta*, **5** 221 (1922).

[2] For determination of uranium in high speed steels, see *Jour. Ind. and Eng. Chem.* **11** 316 (1919); also *Chem. and Met.* **20** 523, 588 (1919); in carnotite, see C. E. Scholl, *Jour. Ind. and Eng. Chem.* **11** 842 (1919). In the presence of H_3PO_4, see Schoep and Steinkuhler, *Bull. Soc. Belg.* **31** 156 (1922). For general survey of uranium methods, see Kern, *Jour. Am. Chem. Soc.* **23** 685 (1901).

[3] Holladay and Cunningham, New York meeting Am. Electrochem. Soc. May, 1923.

[4] Wilhelm Elsholz, *Dissertation*, February 7, 1916, Friedrich Wilhelms Universität, Berlin.

[5] Ewing and Eldridge, *Jour. Am. Chem. Soc.* **44** 1484 (1922); Gustavson and Knudson, *ibid.* **44** 2756 (1922).

CHAPTER XVII

GROUP VI — THE OXYGEN FAMILY

SELENIUM AND TELLURIUM

ON account of the fact that there are few points of resemblance between oxygen and tellurium, some chemists have seen little family relationship between the members of this sub-group. When, however, oxygen is compared with sulfur, and sulfur with selenium and finally selenium with tellurium, a gradual change in physical properties is observed. This proportionate change in physical properties is best seen in Table XXXVIII. While the relationship in this family is not quite so close as in some others, there are numerous striking analogies both in the elements themselves and in their compounds. In general the abundance of these elements in nature decreases with an increase of atomic weight. All four of the elements exist in interesting allotropic modifications, and they each form analogous compounds with hydrogen. All of these hydrides, except H_2O, have offensive odors and acid properties, the strength of the acids decreasing with increase of molecular weight. The hydrides vary widely in stability, H_2O being a stable compound, H_2S and H_2Se much less so, while H_2Te is quite unstable even below zero. The three elements of heavier atomic weight form

TABLE XXXVIII

Physical Properties of the Oxygen Family

	OXYGEN	SULFUR	SELENIUM	TELLURIUM
Atomic Weight . .	16	32.07	79.2	127.5
Melting Point . . .	−227°	114°.5	170°–217°	452°–454°
Boiling Point . . .	−183°	448°	688°	1390°
Specific Gravity (Solid)	1.43	1.96–2.06	4.28–4.80	5.93–6.4
Atomic Volume . .	11	16	18	21
Color (Solid) . . .	Pale Blue	Yellow	Red-Gray	Black

dioxides and all but selenium form trioxides, while derivatives of SeO_3 are well known. Metallic properties of the elements increase with increase of atomic weight. Both selenium and tellurium in the elementary form show a few of the characteristics of the metals. In compounds the metallic nature is less evident, but tellurium forms two classes of derivatives from TeO_2, the tellurites and tetravalent salts. Oxygen and selenium are known to form only one compound each with chlorine, while sulfur and tellurium both form two chlorides.

SELENIUM

History. — Berzelius discovered selenium in 1817 in the deposits from the sulfuric acid chambers from Gripsholm, Sweden. For some time previous to the discovery it had been observed that when sulfur was obtained from a certain pyrite ore, there was formed in the chambers a red deposit which on ignition gave an odor of decayed cabbage. The red substance was supposed to be a form of sulfur containing some tellurium. Berzelius found that it was a new element which resembled tellurium closely and consequently he named the new element selenium, from the Greek word meaning moon, the name being suggested by the analogy of tellurium, the earth element. He studied the element carefully and prepared many of the more important compounds. The chemistry of this element has developed very slowly, but within the last few years there has been considerable interest shown in attempts to find uses for the element and its compounds.

Occurrence. — Selenium must be considered a rare element, although it is found widely distributed in nature. The distinctive selenium minerals are rare, and they are usually selenides, of such metals as lead, mercury, copper, bismuth, and silver. The element is also found in the free state associated with sulfur and as a selenite. The most common occurrence of selenium is in ores in which the element has partially displaced sulfur. Generally the selenium is present in very small proportions, but on account of the fact that enormous quantities of sulfide ores are used, this represents a considerable amount of selenium. It occurs also in small amounts in meteoric iron, in volcanic lavas, and in certain deposits of coal. Traces of selenium have been detected in rain and snow.[1] Even though present in mineral ores in mere traces, it is readily concentrated either in the flue dusts or in the anode mud of the electrolytic refineries. Considerable quantities are known to exist in Hawaii, Japan,

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[1] *Helvetica Chimica Acta* **1** 52 (1918).

the Hartz Mountains, the Vesuvian region, Hungary, Mexico, Australia, Spain, several parts of South America, California, the Paradox Valley, Colorado, and at Thompsons, Utah.

Extraction. — The two general sources of selenium are from the flue dusts of certain metallurgical processes using sulfide ores and from the slimes of the electrolytic refining processes. The rapid development of electrolytic methods has made the latter the most important source of supply at least in the United States. The method used in extraction[1] depends upon the source of material.

To extract from flue dust, grind the material to a fine powder, then fuse in a nickel crucible in the proportion of 300 gram dust, 200 gram Na_2CO_3 and 775 gram Na_2O_2. Add the fusion mixture to the crucible a little at a time, the heat of reaction usually being sufficient to maintain a fusion temperature without the application of external heat. When the crucible is full, cool and disintegrate the melt with water and remove the insoluble material by filtration. Nearly neutralize the filtrate with concentrated HCl and filter off any zinc or aluminium hydroxides. Then add three volumes of concentrated HCl and boil 30 minutes to reduce H_2SeO_4 to H_2SeO_3. Filter off silica, heat to 80°, and add in small quantities two or three times as much Na_2SO_3 as is needed to precipitate the element selenium. Digest at 80° until the selenium has a uniform gray color, filter, and wash thoroughly with hot water. This method removes selenium quantitively from flue dust.

From anode slimes, selenium may be extracted by adding the finely ground material to concentrated HNO_3 which has been diluted with $\frac{1}{5}$ its volume of water. Heat until the reaction is complete, then filter off the insoluble matter on an asbestos pad; evaporate to dryness to expel excess acid, being careful to prevent the vaporization of SeO_2. Take up the residue in 3 : 1 HCl and precipitate the selenium by adding either Na_2SO_3 or SO_2. The reaction is: $H_2SeO_3 + 2\ SO_2 + H_2O = Se + 2\ H_2SO_4$. Filter off the precipitate, and wash thoroughly.[2] Anode slimes are generally rich in both gold and silver, so the extraction of selenium from such material is of minor interest.

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[1] See Dennis and Koller, *Jour. Am. Chem. Soc.* **41** 949 (1919); also *Eng. and Min. Jour.* **106** 443 (1918).

[2] *Eng. and Min. Jour.* **106** 443 (1918).

Another method of extracting selenium is to boil the mud with a concentrated solution of KCN until the solution turns gray, forming KCNSe. This is filtered off, heated with HCl, when selenium is precipitated. This reaction does not yield pure selenium and the large quantity of HCN evolved is troublesome. Sometimes, the slimes which contain precious metals are cupeled to remove the common metals, then the molten metals are treated with sodium nitrate and sodium carbonate, forming a " niter slag " which contains the selenite and tellurite. This slag is skimmed off, cooled, broken up, and leached with hot water.

A method of extracting both selenium and tellurium from either dusts or slimes is described in British Patent 134,536. It consists in fusing the material with lead and NaOH, $NaNO_3$, or Na_2CO_3. The selenium and tellurium compounds are found in the upper layer, from which they may be removed by dissolving in water, neutralizing with acid and precipitating with SO_2. The noble metals may be removed from the lower layer by cupellation.

In nearly all American crude copper bullion there are found both selenium and tellurium in amounts up to 0.3 per cent, or more. This is practically all concentrated in the slimes,[1] from which they are extracted by fusion with $NaNO_3$ and Na_2CO_3, recovery being either from the niter slag or the Cottrell or scrubber sludge. The latter is filter pressed, and either the press cake or the regular flue dust may be roasted at low temperature, the resulting SeO_2 condensing in crystalline form called selenium " whiskers." They are readily soluble in water when fresh, but on standing there is some reduction to metallic selenium. For the precipitation of selenium, SO_2 is passed into the solution, which should contain about 10 per cent of free sulfuric acid and sometimes a little hydrochloric acid. Under these conditions 98 per cent of the selenium is precipitated as the red powder, the reaction being $Na_2SeO_3 + 2\,SO_2 + H_2O = Se + Na_2SO_4 + H_2SO_4$. The sulfur dioxide is carefully purified by thorough scrubbing. Theoretically one pound of sulfur should precipitate nearly a pound and a quarter of selenium, but in actual use 1–2 pounds of sulfur are burned to produce a pound of selenium.

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[1] Merriss and Binder, *Eng. and Min. Jour.* **106** 443 (1918). This article contains flow sheets, showing the purification of both Se and Te.

Selenium prepared from the niter slag may contain considerable tellurium, which may be removed by adding sulfuric acid to the strongly alkaline solution, thus: $Na_2TeO_3 + H_2SO_4$ $Na_2SO_4 + TeO_2 + H_2O$. Separation by electrolysis in a solution of alkali hydroxide or salt has also been proposed.[1]

Selenium is usually sold as the gray powder. Sometimes selenious acid is required, and this is prepared by dissolving selenium in strong nitric acid, crystals of H_2SeO_3 being formed on evaporation. Some sodium selenite is also sold, being obtained by neutralizing a solution of selenious acid and evaporating. Occasionally there is a demand for red selenium. This is prepared from a solution of sodium selenite by acidifying and adding SO_2. The red precipitate is washed thoroughly, filter pressed, and the press cake dried in the dark by a current of cool, dry air. The red modification must be kept in a cool place away from light and air.

The production of selenium in the United States has never been large and has shown marked fluctuations. Table XXXIX shows the approximate production and value of selenium in the United States for several years. It is stated[2] that the industries of this country could produce 300,000 pounds of selenium annually without making any material additions to present plants. Formerly selenium was imported but the rapid growth

TABLE XXXIX

Consumption of Selenium in United States

	DOMESTIC PRODUCTION		IMPORTATION VALUE
	Pounds	Value	
1913	29,097	$46,900	——
1914	22,867	34,277	$363
1915	No record	——	43
1916	No record	——	16
1917	39,630	70,000	302
1918	103,694	206,540	2,236
1919	60,025	125,966	239
1920	92,141	175,508	——

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[1] *Jap. Pat.* 38,085, Feb. 24 (1921).

[2] Victor Lenher, *Jour. Ind. and Eng. Chem.* **12** 597 (1920).

[3] "Selenium and Selenium Salts," *Tariff Information Series*, F. L. 22, p. [illegible] (1921).

lomestic production has stopped the importation and in
1 large shipments were exported.

etallurgy. — Selenium is easily prepared in the elementary
n by the action of reducing agents upon selenious acid. A
am of SO_2 is most commonly used to produce the amorphous
n, but the same result is accomplished by such reagents as
zinc, stannous chloride, potassium iodide, sodium thio-
ate, phosphorous acid, and arsenious acid. Electrolysis of
nious acid also yields the amorphous variety. The element
also be obtained in colloidal form by the action of a solution
O_2 on selenious acid; by reduction of a dilute solution of the
by hydrazine hydrate; or by pouring a solution of selenium
arbon disulfide into a large volume of ether.

roperties. — Selenium is known in several allotropic forms
h are classified in a variety of ways by different authors.
modifications known as the amorphous, vitreous, and soluble
ns may be considered as representing the same allotropic
even though they differ widely in appearance. For these,
nders[1] has suggested the general name "liquid" selenium
use of the fact that they have no definite melting point.
n these forms are heated they begin to soften perceptibly
0°–60°, they become partly fluid at 100°, and fusion becomes
plete at about 220°. After melting the material remains
tic for a long time and shows a distinct metallic luster.
se forms are somewhat soluble in CS_2.

convenient classification of the various forms is as follows: —

Amorphous selenium is obtained by the reduction of a
tion of selenious acid or by almost any method in which
nium forms rapidly from its solution or vapor. When first
ned it is a bright red powder, which may remain suspended
ne liquor for hours. When this powder is heated to about
t becomes darker in color and clots together, forming a soft
s closely resembling the vitreous form in properties. When
rphous selenium is allowed to stand in contact with carbon
lfide, alcohol, benzene, or chloroform, it is transformed into
crystals, slowly in the dark, more rapidly in the light.
ents such as quinoline or aniline convert amorphous sele-
n to the metallic form.

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[1] P. Saunders, *Jour. Phys. Chem.* 4 423 (1900); see also *Physical and*
ical Properties of Selenium, by Marc, published in Hamburg, 1907.

(2) Vitreous selenium is prepared by heating the amorphous form above 217° and cooling rapidly. It is glassy, brittle, and black in mass form, thin layers showing a deep ruby red color. When finely pulverized it forms a red powder which closely resembles the red amorphous selenium. A thin thread of vitreous selenium behaves like other viscous solids.[1] When a load is applied an immediate elastic strain develops and if the strain is continued, permanent distortion results. Deformation takes place more rapidly in light than in the dark. It is a dielectric, being electrified by friction in a manner resembling glass.

(3) Soluble selenium is prepared by the reduction of selenious acid solutions. In this form selenium is completely soluble in water, forming red fluorescent solutions. The solution may be boiled without change, but on standing or the addition of acids or salts the selenium is precipitated in the insoluble form. Colloidal selenium[2] may be prepared by the following steps: dissolve Na_2SO_3 in water and boil for a half minute with an equal quantity of selenium; filter and dilute 1 cc. with a liter of water; add 4–5 drops of dilute sulfuric acid, and stir. The colloidal selenium is orange-yellow to dark red, depending on concentration.[3] The particles are positively charged, while a colloidal solution prepared by the use of hydrazine hydrate contains negatively charged particles. A colloidal solution is also prepared by the electrolysis of a dilute solution of SeO_2, using platinum electrodes.[4]

(4) Red crystalline selenium exists in two crystalline forms, both monoclinic and both somewhat soluble in carbon disulfide. When amorphous selenium is changed to the red crystalline form, some heat is evolved, but the amount has not been determined.

(*a*) When crystallized from hot CS_2 solutions, selenium forms dark red translucent crystals, isomorphous with monoclinic sulfur.

(*b*) From cold CS_2 solutions selenium forms orange-red crystals of a different type.

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[1] *Jour. Proc. Roy. Soc. N. S. Wales* **53** 156 (1919).

[2] Gutbier and others, *Kolloid. Z.* **29** 161, 287 (1921) and **30** 97 (1922).

[3] *Z. Elektrochem.* **25** 80 (1919).

[4] Gutbier and Weise, *Ber.* **52** B 1374 (1919).

(5) Metallic or gray selenium is obtained from any of the other forms by heating to higher temperatures. Best results are obtained by allowing molten selenium to cool to 210° and keeping the material for some time at that temperature. This is the stable form of selenium between ordinary temperatures and the boiling point, 217°. It forms steel-gray hexagonal crystals which are isomorphous with tellurium. When pulverized it forms a black powder, but on fine grinding a red color appears. The change from vitreous or amorphous selenium to the metallic form is accompanied by the evolution of about 55 calories of heat.

When heated in the air, selenium burns with a bright blue flame, forming solid SeO_2 and emitting a disagreeable odor resembling that of rotten horse-radish, the cause of which is not known. Selenium combines directly with hydrogen, oxygen, the halogens, and many of the metals. These compounds are formed less readily than the corresponding sulfur compounds. But the halogen compounds of selenium are not so readily hydrolyzed as are those of sulfur. Selenium is soluble in sulfuric acid, yielding a green solution which is said to contain selenosulfur trioxide of the formula $SeSO_3$. On diluting this solution selenium is precipitated. Nitric acid oxidizes it to H_2SeO_3.

Selenium boils at about 680°, forming a dark red vapor which may be condensed either as scarlet flowers of selenium or shining drops of molten substance. Vapor density measurements indicate the presence of associated molecules at lower temperatures, but at 900–950° the density indicates a molecular structure Se_2 which is retained up to 1800°. Its molecules become monatomic at 2000°. Freezing point determinations indicate a molecule which is approximately Se_8.[1] On the basis of a diatomic vapor the latent heat of vaporization is 135.5 calories per gram, the heat of sublimation is 219.4 calories, and the heat of fusion 83.9 calories.[2]

The ability of selenium to conduct heat varies with the method of preparation of the sample, its age, and the temperature at the time of testing.[3] At 25° vitreous selenium shows a thermal conductivity between 0.000293 and 0.000328 and crystalline

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[1] *Zeit. anorg. Chem.* **102** 215 (1918).

[2] *Jour. Am. Chem. Soc.* **42** 1579 (1920).

[3] *Jour. Proc. Roy. Soc. N. S. Wales* **51** 356 (1917).

selenium between 0.00070 and 0.00183. The conductivity increases with the temperature at which the sample is prepared and decreases with age.

Metallic selenium conducts electricity rather poorly at ordinary temperatures,[1] but at 200° it becomes a fairly good conductor; on the other hand other forms of selenium have their conductivity lowered by a rise of temperature. The change in conductivity is not uniform, but depends not only upon the allotropic form of selenium but also upon the previous treatment of the sample. Exposure to light, even for less than $\frac{1}{1000}$ of a second,[2] produces an increase in the conductivity of granular crystalline selenium; an increase of 15 times or more has been claimed. When the light is shut off, the conductivity decreases rather slowly, reaching normal in a short time. The effect is produced mainly by the red rays, but very feeble beams of light make a notable change. It has been found that the Roentgen rays and radium produce a similar effect. The presence of turpentine, hydrogen peroxide, and various animal and vegetable pigments produce a slight increase in the conductivity of selenium. Many theories[3] have been advanced to account for this phenomenon. It was first suggested that the change in conductivity was due to the heating effect of a beam of light, but later it was found that the temperature of liquid air had little effect upon the phenomenon. Other explanations offered were: (1) the formation of another crystalline form of the element;[4] (2) formation of metallic selenides at the electrodes, this theory being supported by the fact that the use of brass or copper electrodes is found to have a beneficial effect upon the efficiency of the cells; (3) it is suggested that fluorescence may form a connecting link between light and electricity; (4) the catalytic effect of light in favoring certain chemical reactions; (5) polarization between the individual crystals[5] which act as simple cells, the polarization being decreased by illumination; (6) the ionization of the material by light. This latter theory, which seems to be most in favor at present, is due to Fournier D'Albe.

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[1] Bidwell states that selenium may have a resistance as high as 25,000 megohms per cubic centimeter.

[2] Thirring, *Z. techn. Physik* **3** 118 (1922).

[3] W. Späth, *Z. Physik* **8** [3] 165 (1922).

[4] H. Pélabon, *Compt. rend.* **173** 1466 (1921); *ibid.* **174** 391 (1922).

[5] Reichinstein, *Zeit. wiss. Phot.* **17** 16 (1917).

According to this idea light produces an ionization upon the surface of the selenium, hence instantly increasing its conductivity. This theory explains easily why recovery is slow after the light is shut off. It also explains why the deep penetrating Roentgen rays produce a similar effect but with a much slower recovery.

Uses. — The most spectacular uses of selenium are dependent on its change of conductivity when brought from dark into light, although the amount of selenium used in devices of this sort is very small. This property has been known for a long time, since as early as 1873 Willoughby-Smith wrote, concerning his experiences with selenium as an insulator in ocean cables: "By means of a telephone I can hear a ray of light falling on a metal plate." The first successful selenium cells appear to have been prepared by Graham Bell and Sumner Tainter in 1878. Many improvements have since been made by increasing the surface of selenium exposed to the light, thereby reducing materially the resistance to the current and increasing the effect of the light. These cells are of various shapes and forms, but in general they consist of a device [1] for exposing to the light a maximum amount of a thin layer of selenium, giving a minimum distance for the current to pass through the selenium. A very important part in making a cell is to see that the selenium is carefully "annealed" by keeping it for some time at a temperature of about 200° in order to obtain the gray crystalline modification. Sometimes silver is added [2] and the heated material is allowed to cool very slowly to room temperature.

Many suggestions have been made for the application of selenium cells, but few actual uses are found to be practical.[3] It has been used to measure faint sources of light, as from the variable stars,[4] and to turn on and off the light in lighthouses and buoys. It has been suggested also for transmitting photographs or sketches by telegraph; for the production of sounds in moving pictures; for burglar alarms; for exploding torpedoes by a beam of light; for reading by sound; for controlling the time exposure in photography; for automatically recording the

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[1] See *Selenium Cells and How They are Made*, by Samuel Wein, Progress Publishing Company, New York.

[2] *Ger. Pat.* 304,261.

[3] See Edward Cohen, *Mineral Foote-Notes*, Sept.–Oct., 1919, Foote Mineral Company, Philadelphia.

[4] See "Selenium Cell in Practical Photometry." *Trans. Ill. Eng. Soc.* **15** 827 (1920).

density of smoke in flues and reaction chambers, and for a great variety of other more or less utopian purposes. The principle upon which these contrivances operate is the varying intensity of a beam of light. For example, the photophone is arranged to permit a person to telephone along a beam of light. The light falls upon a metal disk like that in the transmitter of a telephone. As the disk vibrates the beam of light is broken up into waves of varying intensities. By directing this fluctuating beam toward a concave mirror the light is focused upon a selenium cell, which when properly connected with a telephone receiver reproduces the original sounds. This is probably the earliest wireless telephone, and has been used over a distance of 230 yards. In 1898 a similar receiving set was used in connection with the speaking arc as transmitter and a conversation was heard at a distance of nearly five miles. In spite of its disadvantages the selenium cell may be found useful in telephony [1] and in controlling many manufacturing processes.[2]

The most practical device of this type at the present seems to be in connection with the lighthouse service, where lights in isolated places are actually regulated by means of the selenium cell. The " tell-tale "[1] which indicates when a ship is off its course ought to be useful. Another application which may be developed through the selenium cell or some similar mechanism is the speaking movie. In the Lauste system [3] the pictures and sounds are recorded on the same film ; the sounds are reproduced by means of a selenium cell and a telephone system. It is claimed that the sounds are reproduced with the utmost fidelity, but the great advantage with this system is the absolute synchronism obtained.

Some of these devices may become useful, the chief difficulty now seeming to be the slow recovery of the maximum resistance in the selenium cell. Experiments have shown [4] that the selenium shows marked fatigue from which it recovers quite slowly, especially after exposure to intense illumination. A serviceable device to overcome this characteristic is to use a series of cells so arranged that while one is in use the others are recovering in the dark.

[1] Thirring, *Z. techn. Physik.* **3** 118 (1922).

[2] Logan, *Jour. Ind. and Eng. Chem.* **15** 40 (1923).

[3] *Sci. Am.* Dec. 22 (1917).

[4] *Elektrotechn. Zeit.* **40** 104 (1919).

Ceramic[1] industries are the main consumers of selenium at the present time, the largest use being as a decolorizer in the manufacture of glass. During the war the shortage of manganese encouraged the use of selenium to correct the green color of glass due to the presence of ferrous iron. It was found that the resulting glass was particularly brilliant and free from impurities. Consequently the use has increased steadily in spite of the prediction that the cost would be prohibitive.[2] In 1921 there was a ready sale for all the selenium produced in this country. The selenium was formerly added as the element, but since the loss is heavy due to its volatility, the addition is now commonly made as an alkaline earth compound. When selenium is added in small amounts, it produces a faint pink color. Since this color is not exactly complementary to the green produced by ferrous iron, a little cobalt oxide or arsenious oxide is also commonly added. A batch of bottle glass composed of 1000 lbs. of sand, 200 lbs. limespar, and 370 lbs. soda ash is decolorized by $\frac{1}{2}$ ounce of selenium[3] and $\frac{1}{12}$ ounce of cobalt oxide. If soda ash is replaced by salt cake a larger amount of selenium is required, and in such a case is best added in the form of Na_2SeO_3. When selenium is added to molten glass the doors of the furnace should be closed securely for a time to prevent the loss of this element by burning out. After the selenium is thoroughly incorporated in the melt, there is little loss up to 1400°,[4] probably due to the fact that it is held in colloidal solution. If larger amounts of selenium are added ruby glass is produced, highly prized for signal lamps because practically all the red rays of light are transmitted while nearly all other wave lengths are eliminated. Selenium is also used in the manufacture of red enamel ware and for the production of enameled steel products.

Experiments have been made in regard to the uses of selenium in vulcanizing rubber. One process[5] adds 28 per cent selenium at a temperature of 160°; 4 per cent naphthylamine is added as an accelerator together with zinc oxide. It is claimed that

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[1] The word "ceramic," as here used, is intended to include glass, glazes, and enamels as well as clay products. This broader interpretation of the word is recommended by a Committee of the American Ceramic Society, *Jour. Am. Cer. Soc.* **3** 526 (1920) and indorsed by W. A. Oldfather, *ibid.* **3** 537 (1920).

[2] See Victor Lenher, *Jour. Ind. and Eng. Chem.* **12** 597; also *Jour. Soc. Jap. Ceram.* **338** 44.

[3] Turner and Cousen, quoted in *Mineral Industry* **30**, 616 (1921).

[4] *Jour. Am. Ceram. Soc.* **2** 895.

[5] *U. S. Pat.* 1,249,272 (1918).

rubber prepared in this way lasts longer than a similar rubber which has been vulcanized with sulfur, but this claim does not appear to be justified. The fact that selenium has a higher melting point than sulfur introduces difficulties when attempts are made to use the former for vulcanizing processes.

A trace of selenium in printers' ink has a remarkable effect in retarding the drying process.[1]

Selenium cells have been suggested as a rectifier.[2] If an alternating current is superimposed upon a direct current passing through a selenium cell, the latter is augmented. A battery has been made capable of furnishing a direct current at 6000 volts when fed by an alternating current.

Selenium has been used experimentally in the palliative treatment of cancer and tumors. Prepared in the ordinary way selenium is distinctly toxic, but electrically prepared colloidal selenium is said to be non-toxic as long as it is not exposed to an acid atmosphere. It is difficult to determine whether this material is successful or not.

Compounds of selenium have been tested experimentally in various ways. Certain selenides[3] have been used in a limited way for treatment of cancer, tumor, syphilis, etc. Only the simplest compounds have been tried and success is not marked. Wasserman has attempted to substitute selenium for sulfur in the manufacture of dyestuffs. The substitution of selenium for sulfur in the preparation of fungicides and insecticides produces a spray, which in some cases seems to be more efficient than its sulfur relative. But in these uses, as in other applications of selenium, the cost of the material makes the utility extremely doubtful. Selenium dioxide has been suggested as a catalyst in the manufacture of sulfuric acid,[4] according to the reaction $SeO_2 + 2\,H_2O + 2\,SO_2 = Se + 2\,H_2SO_4$. The selenium is recovered by filtration and used again, while the selenium in solution in the acid is precipitated by adding SO_2. The value of this process is doubtful because of the fact that the presence of a small trace of selenium in sulfuric acid interferes seriously with certain uses of sulfuric acid. Certain compounds of

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[1] T. W. Anstead, *Chem. and Met. Eng.* **27** 305 (1922).

[2] *Arc. sci. phys. nat.* **44** 472 (1917).

[3] For preparation of metallic selenides in colloidal form, see *Brit. Pat.* 173,507, Dec. 22, 1921.

[4] *U. S. Pat.* 1,341,462.

selenium, especially lead and barium selenite, have been used successfully as paint bases.[1] They are fine grained, are very white, and possess an exceptionally high index of refraction, which gives them an intense opacity.

Compounds. — The compounds of selenium resemble those of sulfur closely. The valence of the element is − 2 in the hydride, + 4 in the dioxide and its derivatives, and + 6 in the selenates. In all of its compounds selenium displays the properties of a non-metal, its acid-forming tendency being marked especially in its higher valence.

Oxygen apparently forms only one well defined compound with selenium, SeO_2, although several others are mentioned. Berzelius states that the characteristic odor of burning selenium is due to the formation of a suboxide SeO. It is suggested[2] also that Se_2O_3 is formed when selenium is dissolved in H_2SeO_4; if such a compound exists it should probably be considered as a selenium derivative of $SeSO_3$, formed when selenium dissolves in H_2SO_4. Selenium trioxide has not been isolated, although derivatives of this compound are well known.

The dioxide is formed[3] by burning selenium in oxygen containing nitrous fumes or by oxidation with nitric acid. Molten sulfur displaces selenium, SO_2 being formed. SeO_2 is a true anhydride, five parts dissolving in one part of hot water; from the crystals of selenious acid SeO_2 is readily obtained by heat.

Selenious acid,[4] H_2SeO_3, resembles sulfurous acid in the method of formation, the nature and kinds of salts formed, and its general behavior with oxidizing and reducing agents. Reducing agents precipitate elementary selenium, rapidly in the presence of heat and sunlight, more slowly in the cold and dark. On exposure to air a colorless solution of selenious acid, soon develops a red tint due to the liberation of red selenium by the dust of the air; this is in marked contrast with the behavior of sulfurous acid, which oxidizes in the air. The selenites of the alkali metals are soluble in water, but those of the other metals are insoluble; the acid selenites are soluble compounds.

Selenic acid, H_2SeO_4, is formed by the oxidation of selenious acid by such reagents as potassium permanganate, chlorine, or bromine. The best method[5] of preparing pure selenic acid is to add pure bromine to Ag_2SeO_3, filter off AgBr, and warm to remove bromine and water. Add H_2S to remove H_2SeO_3 and filter off the precipitated S and Se. The water solution of selenic acid can be concentrated somewhat at ordinary pressures,

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[1] Henry A. Gardner. Circular, No. 62. Educational Bureau of Paint Manufacturers' Association of U. S., Apr., 1919.

[2] Cameron and Macallan, *Proc. Roy. Soc.* **46** 13 (1890).

[3] J. Meyer, *Ber.* **55** B 2082 (1922).

[4] Rosenheim and Krause, *Z. anorg. allgem. Chem.* **118** 177 (1921); Manchot and Ortner, *ibid.* **120** 300 (1922).

[5] *Trans. Wis. Acad. Sci. Arts and Letters* **19** 369 (1918).

but before all the water is driven off the acid begins to decompose, yielding SeO_2, oxygen, and water. By evaporating under diminished pressure nearly anhydrous H_2SeO_4 may be prepared. When the concentrated acid is diluted, much heat is evolved; it also has the power of charring many organic compounds; it forms hydrates corresponding in general to those of sulfuric acid. The hot aqueous solution dissolves gold and copper, being itself reduced to selenious acid; but with the more active metals, it yields selenates and hydrogen. Selenic acid is reduced[1] by H_2S, SO_2, sulfur, and selenium, somewhat slowly at room temperature, but more rapidly in concentrated solution and at higher temperatures. Concentrated HCl reduces it with the liberation of chlorine; consequently, a mixture of selenic acid and concentrated hydrochloric acids will dissolve gold and platinum readily. Nitrosyl selenic acid is formed by the action of liquid N_2O_3 on pure $H_2SeO_4 \cdot H_2O$. It is unstable, decomposing at 80°.[2]

The selenates are formed by oxidation of the selenites or by fusion of selenium or selenium dioxide with KNO_3 or Na_2O_2. They resemble the sulfates remarkably, in hydration, crystalline form, and solubility. Barium selenate, while highly insoluble in water, is reduced with boiling HCl solution, yielding the soluble H_2SeO_3. This treatment reduces all selenates, and consequently it is of value in the detection of selenium in the higher state of oxidation.

Perselenates and perselenic acid are not formed under conditions which are most favorable to the formation of persulfates and persulfuric acid. Complex selenates are known.[3]

Fluorine forms a tetrafluoride, SeF_4, by interaction of the elements at ordinary temperatures and a hexafluoride, SeF_6, when the reaction takes place at −78°. The former is hydrolyzed by water.

Chlorine forms the monochloride, Se_2Cl_2, and the tetrachloride $SeCl_4$. The former is made by passing a current of chlorine over selenium or gaseous HCl into a solution of selenium in fuming nitric acid, or it may be made by passing dry HCl into a solution of selenium in oleum,[4] with gentle heating. It is a brown oily liquid which decomposes on heating, yielding selenium and its tetrachloride; it is hydrolyzed, giving selenious acid and selenium.

Selenium tetrachloride is prepared by the action of chlorine on Se_2Cl_2 or by the reaction: $3\,SeO_2 + 3\,PCl_5 = 3\,SeCl_4 + P_2O_5 + POCl_3$. It is a yellow solid, which sublimes readily and is hydrolyzed by contact with moisture.

Selenium oxy-chloride, $SeOCl_2$, is one of the most interesting compounds which the element forms.[5] It is most easily formed by the reaction of $SeCl_4$ and SeO_2 in carbon tetrachloride or chloroform solutions; it may also be prepared by the partial hydrolysis of $SeCl_4$; or by passing HCl gas into

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[1] E. B. Benger, *Jour. Am. Chem. Soc.* **39** 2171 (1917).

[2] Meyer and Wagner, *ibid.* **44** 1032 (1922).

[3] J. Meyer, *Z. anorg. allgem. Chem.* **118** 1 (1922).

[4] Heath and Semon, *Jour. Ind. and Eng. Chem.* **12** 1100 (1920).

[5] See articles by Victor Lenher and his associates, *Jour. Am. Chem. Soc.* **42** 2498 (1920); *ibid.* **43** 29 (1921); *ibid.* **43** 2378, 2383; *ibid.* **44** 1664 (1922); *Jour. Phys. Chem.* **26** 156 (1922).

SeO_2 at moderately low temperatures, forming $SeO_2 \cdot 2\,HCl$, which on dehydration yields $SeOCl_2$. As usually prepared the oxy-chloride has a yellow color, though the pure compound is nearly colorless. It is a heavy liquid (Sp. gr. 2.44) which boils at 179.5° and decomposes in contact with moisture in the same manner as other acid chlorides. It mixes in all proportions with CS_2, CCl_4, $CHCl_3$, C_6H_6 from which it may be separated by fractional distillation. It dissolves sulfur, selenium, and tellurium readily and reacts with most metals to form chlorides. It dissolves also rubber, redmanol, bakelite, gums, resins, celluloid, gelatin, glue, and asphalt. Possibly its most important properties are from its ability to serve as a selective solvent, in such cases as separation of unsaturated hydrocarbons, with which it reacts vigorously from the saturated series, which react only slowly at high temperatures; it dissolves sugar and starch when warm but has no effect on cellulose; it dissolves the resinous portion of coal, leaving a carbonaceous residue; it dissolves MoO_3, forming a solution which by a reversible photo-chemical action is colorless in the dark but becomes blue in the light; it does not dissolve WO_3, hence it may be used to separate molybdenum and tungsten; in the presence of sulfuric acid it dissolves Cb_2O_5 readily, while Ta_2O_5 is almost insoluble.

Selenium oxy-bromide, $SeOBr_2$, is prepared by the interaction of SeO_2 and $SeBr_4$. It is a reddish-yellow solid, melting at about 41.6° and decomposing at slightly higher temperatures. The liquid is an active solvent and a strong oxidizing and brominating agent.[1]

Hydrogen combines directly with selenium, forming H_2Se. The union takes place slowly below 320°, more rapidly at higher temperature, but as the temperature rises the reverse reaction becomes more apparent. At about 575° the maximum yield of H_2Se is obtained. The best method of preparation is by the action of dilute HCl upon a metallic selenide, such as Na_2Se, $FeSe$,[2] or Al_2Se_3.[3] Hydrogen selenide is a colorless gas, combustible, stable in sunlight, unaffected by dry oxygen, and possesses a persistent and disagreeable odor. Berzelius records[4] that a single bubble of the gas so paralyzed his sensory nerve that he was unable to distinguish the odor of strong ammonia for several hours. The sense of smell returned after five or six hours, but severe irritation of the mucous membrane lasted for a fortnight. The gas dissolves in water at the rate of 3.31 volumes in one volume of water at 13.2°. The solution reddens litmus, absorbs oxygen from the air, precipitating red selenium, precipitates metallic selenides, and is decomposed by sulfur.

Sulfur forms several series of mixed crystals with selenium, but there appears to be no simple compound of these elements.

Selenosulfur trioxide, $SeSO_3$, is formed when selenium is dissolved in fuming sulfuric acid or in sulfur trioxide. It forms a green solution.

Many compounds of selenium, corresponding to well known sulfur compounds, have been prepared, such as: selenosulfuric acid, H_2SeSO_3;

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[1] Lenher, *Jour. Am. Chem. Soc.* **44**, 1668 (1922).

[2] Moser and Doctor, *Z. anorg allgem. Chem.* **118** 284 (1921).

[3] J. R. Pound, *Trans. Chem. Soc.* **121** 941 (1922).

[4] *Lehrbuch 5, Aufl.* **2** 213.

selenotrithionic acid, $H_2SeS_2O_6$; polyselenides, Na_2Se_5, etc. In a great many organic compounds selenium may replace sulfur, giving such compounds as ethyl selenide, ethyl selenic acid, selenurea, etc. Of particular interest are trimethylarsine selenide,[1] $(CH_3)_3AsSe$, and a selenium mustard gas of the composition dichlordiethyl selenide.[2]

Detection.[3]— In the ordinary scheme of qualitative analysis, elementary selenium is precipitated with the sulfides of Group II by H_2S; the precipitate is dissolved in $(NH_4)_2S_x$ and selenium is reprecipitated on acidification. The following are characteristic confirmatory tests:

(*a*) Precipitation of red selenium from cold selenious acid solutions by SO_2, $SnCl_2$, NH_2OH, and other reducing agents. Usually on heating the precipitate turns black.

(*b*) On heating selenium or its compounds an offensive odor, resembling rotten horseradish, is emitted.

(*c*) Metallic selenium dissolves in strong sulfuric acid, giving a green solution. On dilution the color disappears but red selenium precipitates.

(*d*) For the detection of selenium and tellurium from the same sample, saturate the solution with SO_2 and digest the precipitate with potassium cyanide solution. Selenium dissolves and may be reprecipitated by acidification of the cyanide solution; the residue which does not dissolve in cyanide may be tested for tellurium.

Because of the fact that as little as 0.5 milligram of selenium in a liter of sulfuric acid spoils the acid for use in the manufacture of paper, the detection of selenium in sulfuric acid is of special importance. A delicate test for selenium is carried out as follows: dilute a portion of the sulfuric acid, add HCl and SO_2, when red selenium precipitates. The following tests are also recommended:[4] (*a*) a few crystals of KI are added to the sulfuric acid under examination and if selenium is present it is precipitated or iodine is liberated, and may be detected by starch solution; (*b*) a few drops of the sulfuric acid under examination are added to codeine phosphate, when a green or bluish green color indicates the presence of selenium.[5]

Determination. — The gravimetric determination of selenium is carried out by weighing the element on a tared filter. Precipitation is best made with sulfur dioxide or Na_2SO_3 from a solution whose bulk is at least 30 per cent hydrochloric acid; or by an excess of potassium iodide added to a solution containing HCl. In both cases the material should be boiled for 10–20 minutes till the black selenium results, since this form is more easily filtered and washed.

Volumetrically selenium may be determined in several ways:

(1) Selenious acid reacts with a known excess of an iodide, in the presence of arsenic acid, which is reduced to arsenious acid. After boiling to

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[1] Renshaw and Holm, *Jour. Am. Chem. Soc.* **42** 1468 (1920).

[2] Heath and Semon, *Jour. Ind. and Eng. Chem.* **12** 1100 (1920); see also Bogart and Herrard, *Jour. Am. Chem. Soc.* **45** 238 (1923).

[3] See *Compt. rend.* **163** 332 (1916).

[4] See also *Ann. chim. anal.* **23** 25 (1918); C. A. **12** 1028 (1918); Dennis and Koller, *Jour. Am. Chem. Soc.* **41** 961 (1919).

[5] E. Schmidt, *Arch. Pharm.* **252** 161; C. A. **8** 2880 (1914).

remove iodine, the amount of arsenious acid is determined by titration with iodine.[1]

(2) Selenious acid in the presence of HCl is treated with a known excess of $Na_2S_2O_3$, when this reaction takes place : $H_2SeO_3 + 4\ Na_2S_2O_3 + 4\ HCl = Na_2S_4SeO_6 + Na_2S_4O_6 + 4\ NaCl + 3\ H_2O$. The excess thiosulfate is titrated with iodine.[2]

(3) By adding an excess of $KMnO_4$, selenious acid is oxidized to selenic and the excess permanganate determined with oxalic acid solution.[3]

(4) Selenic acid may be reduced to selenious by HCl and the chlorine liberated caught in iodide solution.[4] The electrolytic determination[5] of selenium can be carried out only in the absence of tellurium, and its success is still somewhat doubtful.

TELLURIUM

History. — The early mineralogists were puzzled by a substance which they found in small quantities in various ores. It had a decided metallic luster, but its behavior was distinctly non-metallic. So they called it "aurum paradoxum" or "metallum problematum." In 1782 Reichenstein made a preliminary study of the substance and reached the conclusion that it was a new metal with peculiar properties. Klaproth, in 1798, took up the study of tellurium ores, became convinced that it really was a new element, and suggested the name tellurium, meaning the earth element. Thus the discovery of tellurium preceded by nearly 20 years that of selenium, although the latter is probably more abundant in nature. However, there was almost nothing done toward developing the chemistry of tellurium until Berzelius in 1832 made a much more thorough study of the element and its compounds. He concluded that the substance was essentially a metal, but since its compounds so closely resembled those of sulfur and selenium he placed it in the sulfur group. Because of lack of uses for tellurium and its compounds, its later development has been almost wholly neglected. For a long time after the announcement of Mendeléeff's table the only interest in this element was in connection with its atomic weight. Recently there are indications of revival of interest in connection with tellurium.

Occurrence. — Tellurium like so many of the other rare elements occurs widely distributed in nature, but almost always in small amounts. It is found as native or graphic tellurium, associated with sulfur, selenium, gold, silver, bismuth, copper, and other metals. It also is found in combination with many metals giving such ores as sylvanite $(Au, Ag)Te_2$, petzite $(Ag, Au)_2Te$

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[1] Gooch and Pierce, *Am. Jour. Sci.* (IV) **1** 31 (1896).

[2] Norris and Fay, *Am. Chem. Jour.* **18** 703 (1896) and **23** 119 (1901).

[3] Gooch and Clemons, *Am. Jour. Sci.* (III) **1** 51.

[4] Gooch and Evans, *Am. Jour. Sci.* (III) **1** 400; also *Zeit. anal. Chem.* **57** 277 (1918).

[5] E. Müller, *Zeit. physik. Chem.* **100** 346 (1922).

hessite Ag_2Te, altaite PbTe, coloradoite HgTe, and tetradymite $Bi_2(Te,S)_3$. Telluric ochre or tellurite is impure TeO_2, and a selenide, Te_3Se_2, forms dark gray hexagonal crystals. Montanite, a bismuth tellurate, is found in one locality in Montana.

Tellurium is commonly said to be less abundant than selenium, but this may be due to the fact that no effort has ever been made to collect tellurium from its various sources. The total amount of tellurium in gold deposits alone is probably very large.

The chief sources of tellurium at the present time are the slimes from the electrolytic tanks of the copper and lead refineries and the flue dusts from the smelters using certain ores, especially telluride gold ores. It is estimated [1] that the United States alone could produce annually as much as 125,000 pounds of tellurium without making any material additions to the present plants. The amount actually marketed has been small and subject to material variations. No reliable data are available as to the amount sold.

The price of tellurium appears to be wholly artificial. It is stated [2] that the price during the war was about $3.00 per pound, although as high as $5.00 has been charged. Sales are also recorded as low as 50 cents per pound, and an average price is somewhere around $1.50 to $2.50 per pound.

Extraction. — Tellurium is obtained from the same sources as selenium. The slimes from the electrolytic refining of lead usually yield more tellurium, while the slimes from copper refining are richer in selenium. Tellurium is extracted from flue dusts and slimes by the methods used in the reclamation of selenium, the two elements usually coming out together. Tellurium may be precipitated as TeO_2 from the boiling solution by adding sulfuric acid,[3] according to the reaction $Na_2TeO_3 + H_2SO_4 = Na_2SO_4 + TeO_2 + H_2O$. The addition of the acid must be made slowly, for the solution froths badly and if too much acid is added TeO_2 is redissolved. From the mother liquor selenium is precipitated by adding sulfur dioxide.

Metallurgy. — Metallic tellurium may be prepared from the precipitated tellurium dioxide by either the dry or the wet process. In the former the material is carefully dried, and

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[1] Victor Lenher, *Jour. Ind. and Eng. Chem.* **12**, 597 (1920).

[2] *Min. Ind.*, 1917, p. 619.

[3] Merris and Binder, *Eng. and Min. Jour.* **106** 443 (1918).

mixed with powdered charcoal in the proportion of about 3–5 per cent by weight. The charge is placed in a suitable furnace, carefully covered to prevent loss of tellurium and heated to a temperature between 450° and 500° C. The yield of tellurium may be as high as 95 per cent, but it is sometimes as low as 50 per cent, due largely to loss by volatilization.

In the wet process the TeO_2 is dissolved in strong hydrochloric acid, about 4 pounds of commercial acid being required for each pound of the dioxide. The solution is diluted with water to facilitate the precipitation of the tellurium, but if too much water is added TeO_2 is thrown out of solution. Sulfur dioxide is passed through the solution, and the tellurium is precipitated as a dark gray powder. This is filtered out, dried, and prepared for shipment by grinding to a fine powder or remelting and casting into cakes or sticks.

The dry method is more rapid, but the loss is great and the fumes objectionable. There is little difference between the methods either in cost of operation or in the purity of the product.

Tellurium is also sometimes prepared from the alkaline residues obtained in the process of extracting bismuth from its ores. They are acidified with HCl and tellurium precipitated by sulfur dioxide. From the minerals such as tetradymite, tellurium may be extracted by heating strongly with sodium carbonate and oil. This forms sodium telluride, Na_2Te, which is extracted with water, the tellurium being precipitated by exposure to the air.

Crude tellurium prepared by any of these methods contains many impurities. To obtain pure tellurium the crude material is dissolved in aqua regia, and the excess nitric acid expelled by hydrochloric acid. Dilute so as to precipitate $PbCl_2$, which is filtered out, and the tellurium is precipitated from the filtrate by means of SO_2. This is then fused with potassium cyanide and the melt is extracted with water, and after filtering, tellurium is precipitated from the clear solution by a stream of air. Finally the powder is melted and distilled in an atmosphere of hydrogen.

Purification may also be brought about by boiling the crude tellurium with sodium sulfide and powdered sulfur. On adding sodium sulfite, pure tellurium is thrown down as a dark gray powder.

Properties. — Tellurium is commonly described as giving several allotropic forms,[1] but these are doubtful. A form of tellurium sometimes described as amorphous is obtained by the reduction of tellurous or telluric acid by sulfur dioxide, hydrazine hydrate, hydroxylamine, or other similar reagent. It is probable that this is not a distinct allotropic form, but that it is a finely divided condition which corresponds to the powder formed by most of the elements. Powdered tellurium is a fine black powder with a specific gravity of 6.015. On heating it becomes crystalline, heat being evolved.[2] Crystalline tellurium is silvery-white in color, possesses a decided metallic appearance, and is so brittle that it may easily be ground to a powder. It is a poor conductor of heat and electricity, its conductivity varying only slightly with change of illumination. It has a specific gravity of 6.27, melts at 452°, and boils [3] at about 1400°, giving a vapor with a golden-yellow color. The molecular weight of tellurium corresponds to the formula Te_2. Its crystals are rhombohedric in form and are insoluble in water and carbon disulfide, but soluble in nitric acid, strong sulfuric acid, and aqua regia. Hydrochloric acid does not attack it, but it dissolves in hot alkali solutions, forming both tellurides and tellurites. At ordinary temperatures tellurium remains unchanged in the air or in oxygen, but on heating it burns with a blue (or green) flame, forming TeO_2. Colloidal tellurium may be prepared by the reduction of telluric acid or by electrolysis of a solution of tellurium in nitric acid.

Tellurium gives a most peculiar and characteristic effect when introduced into the animal body through the lungs, stomach, or skin. Even in small amounts it produces a tellurium breath which is both offensive and persistent. The objectionable odor is also shown in the perspiration.

The atomic weight of tellurium has furnished a problem of keen interest to chemists. Its close relationship to sulfur and
ire its location in the Periodic Table in Group VI,
iodine. But the atomic weight determinations
a value of 127.5 and iodine 126.92. Because

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c allotropy of tellurium see Cohen and Krimer,
13) and A. Damiens, *Compt. rend.* **174** 1344 (1922).
174 1548 (1922).
e boiling point is found to be 478° according to

of this apparent discrepancy many efforts have been made to find in tellurium an unknown element of higher atomic weight.[1] This possibility has seemed inviting also because of the fact that in Group VII there is room for three elements now unknown. Although some workers have reported results which give tellurium a lower atomic weight than iodine, other investigators[2] have failed to confirm these conclusions. The determination of the atomic numbers has shown that tellurium should be placed before iodine in spite of its higher atomic weight.

Uses.[3] — Tellurium has for some time been known as the useless element because there have been so few applications for it in the industries. Its resistance to acid corrosion has suggested that it might be serviceable as an alloying element in the preparation of resistant alloys, but none seem to have been successful. It alloys with lead without difficulty,[4] increasing hardness and brittleness. It alloys also with tin, increasing the tensile strength materially but increasing its hardness only slightly. An alloy of zinc and aluminium with a small amount of tellurium has been prepared. It may be rolled into sheets, giving a firm metal for which great merit is claimed. These alloys appear to be of little value. As far as now known the action of tellurium forms a telluride with the metal, and these tellurides appear to be only slightly soluble in the molten mass. Tellurium has an electrical resistance of 200,000 microhms per centimeter cube, the highest of any metal. Consequently, its alloys may become useful as high resistance material. Tellurium has been used in a limited way for the coloring of glass or porcelain, producing brown, blue, or red under various conditions. In acid solution it is used as a dip for silver ornaments, giving a finish similar to that obtained by dipping in a platinum solution. A solution of tellurium in sodium sulfide is used in toning photographic prints. Tellurium dioxide dissolved in hydrochloric acid is used to number the inner stems of electric

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[1] Steiner, *Ber.* **34** 570 (1901); Flint, *Am. Jour. Sci.* (iv) **28** 347 (1909) and **30** 209 (1910).

[2] Baker and Bennett, *Jour. Chem., Soc.* **91** 1849 (1907); Marckwald, *Ber.* **40** 4730 (1907) and **43** 1710 (1910); Lenher, *Jour. Am. Chem. Soc.* **30** 741 (1908) and **31** 20 (1909).

[3] See Serial 2385, *Tellurium and its Uses*, by H. A. Doerner, U. S. Bureau of Mines.

[4] Ransom and Thieme, *Chem. and Met.* **25**, 102 (1921); Preifuss, *Zeit. elektrochem.* **28** 100, 224 (1922).

light bulbs, heat producing the metal, which marks the glass permanently. The similarity of tellurium to selenium and sulfur suggests the use of the former in the dye and drug industries. The alkali tellurides are effective remedies against excessive perspiration, but their use has not been popular because of the offensive odors produced especially in the breath and perspiration. These compounds also produce marked physiological effects similar to those of arsenic.[1] They have been tried as a cure for cancer, tumor, syphilis, etc., but the results are not convincing.[2] Since tellurium dioxide is decomposed at red heat it becomes a powerful oxidizing agent, so its use has been suggested in the manufacture of sulfuric acid,[3] and in combustions.[4] Recent investigations have shown that tellurium crystals are useful in the detectors for wireless telephones. The popularity of wireless equipment is shown by the fact that a single company has sold [5] over a ton of tellurium for this purpose, although each instrument requires only a few grams of the element. The most interesting application yet suggested is as an anti-knock agent to be added to gasoline.[6] It has been found that the addition of a small per cent of diethyl telluride to gasoline permits the use of high compression motors, by means of which the mileage obtainable is increased as much as 100 per cent. A decided disadvantage in the use of this compound comes from its persistent and unbearable odor. If some method can be found to overcome this obstacle this device would not only serve to use large quantities of tellurium but it would also tend to conserve the supply of gasoline. It is estimated that to "tellurize" all the gasoline now used in automobiles would require 1500 tons of tellurium per year.

Compounds. — The compounds of tellurium resemble those of sulfur and selenium quite closely, but it is somewhat more metallic than either of these elements. It seems logical to expect the oxygen compounds of tellurium to be easily reduced, but it is found that the compounds of selenium are more easily reduced than either the sulfur or tellurium compounds.[7]

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[1] William J. Gies, *Merck's Archives*, June, 1901.
[2] Lenher, *Jour. Ind. and Eng. Chem.* **12**, 597 (1920).
[3] *Zeit. angew. Chem.* **34** 154, 157, 162 (1921).
[4] *U. S. Pat.* 1,341,462.
[5] *Chem. and Met. Eng.* **27** 640 (1922).
[6] Midgley and Boyd, *Jour. Ind. and Eng. Chem.* **14** 849 (1922).
[7] Benger, *Jour. Am. Chem. Soc.* **39** 2179 (1917).

Oxygen forms three oxides, TeO, TeO_2, and TeO_3. The first two are somewhat basic in nature and are represented by numerous salts in which tellurium is bivalent or quadrivalent, respectively. The dioxide and the trioxide are both mainly acidic in character, although a few hexavalent salts of tellurium are known.

Tellurium monoxide, TeO, is obtained by heating $TeSO_3$ in a vacuum to 230°, sulfur dioxide being evolved. It is amorphous, brown to black in color, and is easily oxidized.

Tellurium dioxide, TeO_2, forms when tellurium is burned in the air. It forms white crystals, which melt and boil without decomposition. They are only slightly soluble in water, but react readily with the fused alkalies, forming tellurites. Tellurous acid, H_2TeO_3, is formed by acidifying the solution of an alkali tellurite or by dissolving tellurium in nitric acid, when an unstable nitrate is formed from which tellurous acid separates as a voluminous white precipitate when the solution is poured into water. The tellurites of the alkali metals are best prepared by fusion of TeO_2 in caustic alkali; concentrated solutions of the alkalies dissolve TeO_2 rather slowly, while dilute solutions are almost without effect. The tellurites of the heavy metals are insoluble in water but soluble in hydrochloric acid. The tellurites are usually of complex character rather than of the simple character of the analogous sulfites. Oxidizing agents transform tellurous acid to telluric acid; tellurium is precipitated by sulfur dioxide but not by ferrous sulfate.

Tellurium trioxide, TeO_3, is made by carefully heating H_2TeO_4 to a red heat. It is an orange-yellow crystalline substance, sparingly soluble in water, and easily decomposed by heat, forming the dioxide and oxygen.

Telluric acid, $H_2TeO_4 \cdot 2\,H_2O$ or H_6TeO_6, is made by oxidizing tellurous acid, best by CrO_3, or the chlorates;[1] by the action of an acid on a tellurate; or by the oxidation of $TeCl_4$ by chlorine.[1] It differs markedly from sulfuric and selenic acids by being a solid, much less soluble in water and much less completely ionized. As an acid it is very weak, much like boric or hydrocyanic acid, the ionization[2] constant of a normal solution being 1.6×10^{-4}. It forms various hydrates, it undergoes polymerization readily, forming colloidal or semi-colloidal substances, and crystallizes with such salts as phosphates, arsenates, iodates, and oxalates. In aqueous solution telluric acid is reduced by such reagents as sulfur dioxide, hydrazine hydrate, hydroxylamine, hydrogen sulfide, and hypophosphorous acid.

When the hydrated telluric acid is heated to 160° water is expelled and a white powder known as allo-telluric acid[3] is formed. It is difficultly soluble in cold water, but it dissolves readily in hot water, and from the solution the hydrated acid crystallizes. The allo-acid is a much stronger acid than the hydrated acid. The formula $(H_2TeO_4)_x$ has been suggested for allo-telluric acid, which indicates that it bears to telluric acid the same relationship which meta-phosphoric acid bears to its ortho-acid.

The tellurates may be prepared by fusion of tellurium or its dioxide with

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[1] Meyer and Moldenhauer, *Zeit. anorg. allgem. Chem.* **119** 132 (1921).

[2] Rosenheim and Gerhart, *Jour. Chem. Soc.* **114**, II, 194 (1918).

[3] Mylius, *Ber.* **34** 2208 (1901); Gutbier, *Zeit. anorg. Chem.* **32**, 96 (1902).

an alkali carbonate-nitrate mixture, $Te_2 + K_2CO_3 + 2\,KNO_3 = 2\,K_2TeO_4 + N_2 + CO$. The same results are obtained by passing chlorine into an alkaline tellurite, $K_2TeO_3 + 2\,KOH + Cl_2 = K_2TeO_4 + 2\,KCl + H_2O$. The alkali tellurates are in general soluble in water, while the tellurates of the other metals are sparingly soluble in water but soluble in hydrochloric acid. On heating, a tellurate loses oxygen and forms a tellurite.

Hydrogen forms the telluride, H_2Te, by direct union of the elements[1] or by the action of acid on the tellurides of magnesium, zinc, or aluminium. It is a gas with an offensive odor, but its physiological action is much less marked than is that of hydrogen selenide. The hydride of tellurium is extremely unstable, being decomposed rapidly by temperatures above 0°, or by moist air. Unless it is thoroughly dry, H_2Te is decomposed by sunlight or ultraviolet light; it is more stable in red light. It burns easily with a blue flame, yielding TeO_2 and water. It is soluble in water, and from the solution tellurium is precipitated by the absorption of oxygen from the air. The solution precipitates many metallic tellurides when it is added to the soluble salts of the metals.

The tellurides may be prepared in many cases by heating tellurium with the metal whose telluride is desired. The reaction between molten aluminium and tellurium is especially satisfactory, and aluminium telluride is recommended as a convenient method of producing hydrogen telluride.[2] Molten magnesium reacts vigorously, even explosively, with tellurium. Potassium telluride, K_2Te, is obtained in an impure form by melting together tellurium and potassium cyanide. Sodium and tellurium unite directly to form Na_2Te and complex compounds containing more tellurium.[3]

Fluorine forms the tetrafluoride, TeF_4, by direct union of the elements or by the action of hydrofluoric acid upon TeO_2. The hexafluoride, TeF_6, is formed by the action of fluorine upon tellurium at − 78°. It is completely decomposed by water.

Chlorine combines directly with tellurium even in the cold, forming both $TeCl_2$ and $TeCl_4$. The dichloride boils at 327° and so may be separated from the tetrachloride (B. P. 380°) by careful distillation. Water decomposes $TeCl_2$, thus, $2\,TeCl_2 + 3\,H_2O = Te + H_2TeO_3 + 4\,HCl$. The tetrachloride is probably best formed by the action of sulfur monochloride on tellurium.[4] It is extremely hygroscopic and is decomposed by cold water. Tellurium forms no oxychloride.[5]

Bromine unites directly with tellurium, forming both $TeBr_2$[6] and $TeBr_4$.

Iodine and tellurium do not unite directly[7] even though they are melted together in all proportions, but TeI_4[8] is produced by the action of HI upon tellurous acid, $H_2TeO_3 + 4\,HI = TeI_4 + 3\,H_2O$. Tellurium di-iodide has

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[1] Moser and Ertl, *Zeit. anorg. allgem. Chem.* **118** 269 (1921).

[2] Liddell, *Chem. and Met.* **25** 268 (1921).

[3] Kraus and Chiu, *Jour. Am. Chem. Soc.* **44** 1999 (1922).

[4] Lenher, *ibid.* **24** 188 (1902).

[5] Lenher, *ibid.* **31** 243 (1909).

[6] *Bull. Soc. Chim.* **29** 1063.

[7] Gutbier and Flury, *Zeit. anorg. Chem.* **32** 108 (1902).

[8] A. Damiens, *Compt. rend.* **172** 1105 (1921).

been described, but it is probably a mixture of the elements or of tellurium and TeI_4.[1]

Sulfides of tellurium have been reported by various workers, several formulæ being given for the precipitates formed when hydrogen sulfide is passed into a solution of an alkali tellurite or of telluric acid. These precipitates give up most of their sulfur to carbon disulfide, consequently it has been argued that the precipitates are mixtures of tellurium and sulfur. Snelling[2] claims to have isolated TeS, but Hageman[3] denies the existence of such a compound but claims that H_2S precipitates TeS_2 as a red-brown powder, which is stable only at temperatures below − 20°.

Tellurium sulfoxide, $TeSO_3$, may be made by direct union of tellurium and sulfur trioxide or by dissolving tellurium in strong sulfuric acid with gentle warming. It forms a red solution which on further heating yields a colorless solution, which is the basic sulfate. The sulfoxide forms a red amorphous solid, which on heating to 230° loses SO_2 and leaves behind TeO.

Organic acids like tartaric and citric dissolve tellurium oxide, forming acid salts, $Te(HC_4H_4O_6)_4$ and $Te(HC_6H_9O_7)_2$.[4] Oxalic, lactic, malic, and gallic acids dissolve appreciable amounts of tellurium dioxide, but the tellurium salts of these acids have not been isolated. Succinic acid does not dissolve TeO_2, and the existence of tellurium oleate and stearate is doubtful.

Detection. — Tellurium is precipitated by hydrogen sulfide along with selenium and the sulfides of the second group. At room temperature the precipitate consists of a mixture of tellurium with varying proportions of sulfur; it resembles stannous sulfide in appearance. It is readily soluble in ammonium sulfide and from this solution it is reprecipitated by acids. Tellurium is readily separated from all elements whose compounds are not easily reduced by passing sulfur dioxide into a solution containing a small amount of hydrochloric acid. Probably the best method for the separation of selenium and tellurium comes from the fact that the former is precipitated by SO_2 and other reducing agents from strongly acid solutions, while the latter is reduced to the elementary state from faintly acid solutions only. The addition of KI to a tellurium solution containing a little free HCl gives at first a black precipitate of TeI_4 which dissolves in excess of KI, forming K_2TeI_6, a deep red solution, from which SO_2 precipitates tellurium readily. Under similar treatment a selenium compound is immediately reduced to red selenium on the addition of KI.

Estimation.[5] — Gravimetrically tellurium may be weighed either as the element or as the dioxide. For the former method, nitric acid must be removed by evaporation with hydrochloric acid; then the residue is taken up with dilute HCl, sulfur dioxide bubbled through the solution and tellurium collected and dried on a tared filter paper. For weighing as the oxide, the precipitated tellurium is dissolved in nitric acid containing a few drops

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[1] *Compt. rend.* **171** 1140 (1920).

[2] W. O. Snelling, *Jour. Am. Chem. Soc.* **34** 802 (1912).

[3] A. M. Hageman, *ibid.* **41**, 329 (1919).

[4] A. M. Hageman, *ibid.* **41** 342 (1919).

[5] See the excellent summary of methods by Victor Lenher, *Trans. Am. Inst. of Min. and Met. Eng.*, Feb., 1923; abstracted *Min. and Met.* **4** 32 (1923).

of sulfuric acid, the solution is evaporated to dryness, and the residue ignited gently in a crucible. The basic acetate separation[1] precipitates TeO_2 quantitatively in the presence of selenium, but it does not separate bismuth and copper completely. If a solution containing tellurium is strongly acidified with HCl, then heated to boiling and hydrazine hydrochloride and sulfur dioxide added, tellurium is completely precipitated.[2]

Volumetrically tellurium may be determined by several methods: (1) Tellurous acid is oxidized to telluric by permanganate either in acid solution[3] or alkaline solution.[4] (2) Tellurous acid in hydrochloric acid solution is reduced by an excess of standard stannous chloride, according to the reaction: $TeCl_4 + 2\,SnCl_2 = Te + 2\,SnCl_4$. The excess stannous chloride is determined iodometrically.[5] (3) Telluric acid may be reduced to tellurous by the use of potassium bromide in sulfuric acid solution, thus: $H_2TeO_4 + 2\,HBr = H_2TeO_3 + H_2O + Br_2$. The bromine is distilled into a solution of potassium iodide, the liberated iodine being determined by standard thiosulfate.[6]

The electrolytic determination of tellurium has been suggested,[7] but it is only possible in the absence of selenium, and its success is doubtful.

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[1] Browning and Flint, *Am. Jour. Sci.* **28** 112 (1909).

[2] Lenher and Homberger, *Jour. Am. Chem. Soc.* **30** 387 (1908).

[3] Brauner, *Monat für Chemie* **12** 34 (1892).

[4] Norris and Fay, *Am. Chem. Jour.* **20** 278 (1898); Gooch and Peters, *Am. Jour. Sci.* **8** 122 (1899).

[5] Brauner, *Zeit. anal. Chem.* **30** 707 (1891).

[6] Gooch and Howland, *Am. Jour. Sci.* (III) **48** 375; *Zeit. anorg. Chem.* **7** 132 (1894).

[7] E. Müller, *Zeit. physik. Chem.* **100** 346 (1922).

CHAPTER XVIII

GROUP VIII — THE PLATINUM METALS

In Mendeléeff's table, Group VIII was distinctive from the fact that in place of a single element in each series there were blanks in all series except the fourth, sixth, and tenth, and these spaces were occupied by triads, which showed some striking analogies. Not only do the members of each triad show closely related properties, but their atomic weights and atomic volumes are much closer together than is usual in successive elements. This similarity is not only true of physical properties, but it is so strikingly true of the chemical properties that the separations of members of each of these triads are among the more difficult operations of analytical chemistry.

In addition to the resemblance within the triads themselves, there is also a certain similarity between each element and the corresponding element in the other triads. Thus iron, ruthenium, and osmium have certain peculiar properties in common; cobalt, rhodium, and iridium are somewhat alike, and nickel, palladium, and platinum present similar peculiarities. The resemblances in these vertical triads are especially striking between the last two members, but it is perhaps to be expected that the first member of such a group would differ somewhat from the other members.

The elements of Group VIII form a transition series between the members of the even series and those of the following odd series in much the same way that the members of the Zero Group do between the odd and the following even series. They show properties suggestive of manganese, chromium, molybdenum, and tungsten as well as copper, silver, and gold.

The principal physical properties are shown in Table XL. It is to be observed that there are close resemblances within the triads, although there is considerable departure from the order of atomic weights. Among the notable facts are to be observed the high melting points and boiling points and the high density of osmium, iridium, and platinum. Under certain conditions osmium has the highest density of any known substance.

TABLE XL

Physical Properties of the Platinum Metals

	Atomic Weight	Mean Specific Heat 0–100°	Mean Atomic Heat	Melting Point[1] C°	Boiling Point[2] C°	Density	Coefficient of Expansion
Iron . .	55.84	0.119	6.64	1505	2450	7.84	$0.0_4 12$
Cobalt . .	58.97	0.108	6.37	1489	2415	8.8	$0.0_4 1208$
Nickel . .	58.68	0.109	6.40	1452	2340	8.3–8.8	$0.0_4 1248$
Ruthenium	101.7	0.0611	6.21	>1950	2520	12.	——
Rhodium .	102.9	0.058	5.97	1940	2500	11–12	$0.0_4 058$
Palladium.	106.7	0.059	6.30	1542	2540	11.4–12	$0.0_4 12$
Osmium .	190.9	0.0311	5.94	ca 2700	——	21.3–24	——
Iridium .	193.1	0.0323	6.24	2360	2550	22.4	$0.0_4 07$
Platinum .	195.2	0.0323	6.31	1755	ca 3900	20.9–21.7	$0.0_4 1$

The metals of this group are all white and remain untarnished in dry air. Iron is unique in that it oxidizes readily in moist air, while the other metals either tarnish superficially or are entirely unchanged. These metals, especially in colloidal form or in the finely divided state, are the best catalysts known. They are such active catalysts that so small a quantity as 0.002 mg. of platinum, 0.005 mg. of iridium, 0.0009 mg. of rhodium, or 0.0005 mg. of palladium may be detected on asbestos fiber by heating to redness in a flame and holding in a mixture of coal gas and air. The metallic particles become incandescent because of their activity in promoting the reaction between these two gases. Some of these metals also show the property of selective absorption of gases to a remarkable degree. All these metals form organo-metallic compounds, a fact which contrasts them with the other members of the even series. There is also a marked tendency to form complex radicals, both basic and acidic, from which extended series of compounds are derived, the properties

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[1] The melting points are those given in *Recueil de Constantes Physiques* (1913).

[2] The boiling points are to be considered as only approximately correct.

of which are entirely different from the properties of the corresponding metallic salts.

A comparison of the compounds of iron, ruthenium, and osmium shows many points of resemblance. All three metals form dichlorides, MCl_2, and trichlorides, MCl_3. Complex chlorides are known, such as chlorruthenites, M_2RuCl_5; chlorosmites, M_3OsCl_6, and chlorosmates; iron is commonly said to form no such derivatives, but the double salts like $FeCl_3 \cdot 2\,KCl \cdot H_2O$ may be written K_2FeCl_5 and regarded as chloroferrites. The only oxide common to the three metals is the sesquioxide, M_2O_3. The monoxide, MO, is common in iron, uncertain in ruthenium, and probable in osmium. Both ruthenium and osmium form dioxides, MO_2, but iron dioxide is only known in the ferrites such as $BaFeO_3$. Ruthenium and osmium are the only members of Group VIII which form oxides of the formula, MO_4, although the Mendeléeff table would lead to the conclusion that this should be the common oxide. Both these oxides are volatile, and soluble in water, but neither forms hydroxides nor are they acidic in nature, although almost invariably the higher oxides of the metals show more or less striking acid properties. Ruthenium and osmium form ruthenocyanides, $M_4Ru(CN)_6$, and osmocyanides, $M_4Os(CN)_6$, isomorphous and similar to the ferrocyanides, but neither forms a series analogous to the ferricyanides.

A comparative study of cobalt, rhodium, and iridium reveals some interesting comparisons. Cobalt is almost wholly bivalent in its simple salts, the only stable trivalent derivatives being complex salts like the cobaltinitrites and -cyanides. On the other hand rhodium and iridium are generally trivalent. Accordingly the stable simple chlorides are $CoCl_2$, $RhCl_3$, and $IrCl_3$. From the last two are derived the double chlorides, chlorrhodites, M_3RhCl_6, and chloriridites, M_3IrCl_6; cobalt forms double halides such as $CoNaF_3$ and $CoLiCl_4$. Iridium forms a tetrachloride, $IrCl_4$, from which are derived the chloriridates, M_2IrCl_6. Cobalt alone forms a monoxide, but all three metals form the sesquioxide, M_2O_3, and dioxide, MO_2. The latter are slightly acidic in character, forming cobaltites, rhodites, and iridites respectively; these are analogous to the ferrites, ruthenites, and osmites, and suggest at least a distant relationship to the chromites and manganites. Cobalt, rhodium, and iridium form simple sulfates, M'_2SO_4, alums, $M'M'''(SO_4)_2 \cdot 12H_2O$, and double cyanides, $M'_3M(CN)_6$, but cobalt is the only one which gives $M'_4M(CN)_6$. All three metals form ammino-derivatives similar to those of palladium and platinum. A striking similarity is also found in the double nitrites, $M'_3Co(NO_2)_6$, $M'_3Rh(NO_2)_6$, and $M'_3Ir(NO_2)_6$. The potassium salts of the first two are relatively insoluble, but the last is somewhat more soluble.

Nickel, palladium, and platinum resemble the preceding elements, cobalt, rhodium, and iridium, respectively, and there are also similarities to copper, silver, and gold. Nickel and platinum occlude hydrogen at ordinary temperature, but this property is most prominent in palladium, which can absorb as much as 850 volumes of the gas. All three metals yield a dichloride, and both palladium and platinum form double chlorides, M'_2MCl_4, while nickel may not. Palladium and platinum also form trichlorides[1] and double salts M'_2MCl_5 and $M'MCl_4$; nickel produces no parallel compounds. All three metals have monoxides, MO, and dioxides, MO_2, nickel and platinum have oxides, M_3O_4, and only platinum has a sesquioxide. The dioxides of nickel and platinum display feeble acid properties. All three metals, when in the finely divided state, absorb CO, but no carbonyl compounds of palladium or platinum have been isolated; they all form double cyanides like $K_2M(CN)_4$. Nickel and palladium are readily precipitated by dimethylglyoxime; platinum precipitates incompletely and only on boiling.

The rare elements of Group VIII are collectively referred to as the "Platinum Metals." For convenience they are divided into the Light Platinum Metals or Ruthenium Group and the Heavy Platinum Metals or the Osmium Group. The light metals are characterized by the fact that they combine more readily with oxygen than do the heavy metals, osmium being the only one of the latter which burns in air. Palladium is the only one which dissolves in hot HNO_3. Aqua regia dissolves osmium, forming OsO_4, and platinum, giving $PtCl_4$; it attacks ruthenium slowly, while iridium and rhodium are not appreciably attacked. All the compounds of these metals are easily reduced, consequently the elementary state is the common form in nature.

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[1] According to Fremy's *Encyclopedia* $PdCl_3$ has not been prepared.

While the members of the platinum group resemble one another in a very intimate manner, there are many points of dissimilarity to be observed. If the elements were to be arranged in order showing the most gradual changes in chemical properties the order would probably be

Os — Ru — Rh — Ir — Pt — Pd.

In this arrangement each element resembles its neighbors, but between the extreme elements there is noticeable divergence. This order is difficult to harmonize with the other parts of the periodic table.

THE PLATINUM METALS

History. — It is impossible to tell when mankind first began to use the platinum metals, for they attracted the attention of early races because of their simple metallurgy, bright and permanent color, and their high melting points. Berthelot describes[1] an alloy of platinum, gold, and iridium which was used in forming hieroglyphics at Thebes in the seventh century B.C. Pliny speaks of "aluta," which is supposed to refer to platinum, a name which is derived from platina, a diminutive for the Spanish word plata, silver. About the middle of the sixteenth century, the Europeans were somewhat familiar with a metal from Mexico which they were unable to melt. In 1750 Brownrigg for the first time described the compact metal and termed it a "semi-metal" because of its peculiar properties. Many investigators studied this substance, each adding a few facts concerning its behavior. It appears to have been melted first about 1758; in 1772 it was hammered into foil and drawn into wire. The use of the oxy-hydrogen blowpipe in melting platinum was introduced during the first decade of the nineteenth century by Robert Hare of Philadelphia, the inventor of the blowpipe. In 1859 Debray and Deville first used a lime crucible and cover in fusing platinum. The early work was done almost entirely on South American platinum, which was difficult to obtain because the Spanish government forbade its exportation in order to prevent its use as an adulterant for gold coins. All the early references[2] to platinum refer to a mixture of the metals of this group, usually with some gold, silver, and other metals. The first companion metal to platinum was discovered in 1803.

The discovery of platinum in the Ural Mountains was made in 1819, but it was not until 1824 that its exportation was begun. These deposits developed rapidly and soon became the most important source of supply. In 1828 Russia began to use platinum coins, but the wide fluctuation in the value of platinum caused the discontinuance of platinum coinage in 1845.

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[1] *Compt. rend.* **132** 729 (1901).

[2] For a complete bibliography of the Platinum Metals from early time to the end of 1917 see *Bull.* 694, *U. S. Geol. Surv.* There is, also, an excellent bibliography in *Les Métaux Précieux* by Jean Voisin, *Encyclopédie de Chimie Industrielle* (1922).

About the year 1803, several chemists examined the residue which remains as a black powder when platinum ore is dissolved. This had always been considered as composed mainly of plumbago, but it was found to contain a new metal. In 1804 Tennant[1] announced the discovery of two new metals from this residue. For one he suggested the name *iridium*, the rainbow element, "from the striking variety of colors which it gives while dissolving in acid." The other he named *osmium*, from the Greek word meaning odor, a name suggested by the sharp smell of the volatile oxide. Following this announcement by only a few days, Wollaston described[2] a method of separating still another element from the mother liquor after a solution of platinum salts had been precipitated by ammonium chloride. This new metal formed salts whose solutions even when dilute were rose-red in color, so he suggested the name *rhodium*, rose-colored. Wollaston also discovered the metal *palladium* while he was purifying a quantity of crude platinum. The actual discovery was made in 1803, but the announcement was first made anonymously in the form of an advertisement of a quantity of "palladium or new silver" for sale. The "new metal" was thought to be a fraud composed of an amalgam of platinum. Later Wollaston declared[3] that he was the discoverer, gave his method of reclaiming palladium from platinum ore, and explained that the element had been named in honor of the planetoid Pallas, discovered in 1802.

The last member of the platinum metals to be discovered was *ruthenium*. This element was announced by Osann in 1828, who claimed to have found three new metals in some crude platinum ore from the Ural Mountains. To one he gave the name ruthenium, from Ruthenia, a name for Russia. He soon became convinced that one of the metals did not exist and for some time the others were considered to be mixtures of the oxides of titanium, iron, zirconium, and silicon. In 1845 Claus examined similar ores and found[4] that they contained a new metal for which he retained the name of ruthenium.

Occurrence. — The platinum metals are found native, almost always associated with each other, and generally with small amounts of gold, copper, silver, nickel, iron, and other metals. The grains are small, rarely in nuggets, and are found in alluvial deposits which result from the disintegration of basic igneous rocks. Only a very small part of the world's supply is derived from any other source than alluvial deposits. Iridosmine is a natural alloy of iridium and osmium containing small amounts of the other metals. Alloys of gold with both palladium and rhodium are found occasionally. The platinum metals are found in small amounts in copper ores such as tetrahedrite and

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[1] *Phil. Trans. Roy. Soc.* **94** 411 (1804).
[2] *Phil. Trans. Roy. Soc.* **94** 419 (1804).
[3] *Phil. Trans. Roy. Soc.* **94** 428 (1804) and *ibid.* **95** 316 (1805).
[4] *Annalen* **56** 257 (1845) and *ibid.* **59** 234 (1846).

are reclaimed from this source from the electrolytic sludge. Platinum is also found in certain deposits of coal and its presence has been detected in a certain meteorite.

A few compounds of the platinum metals are met, but always in rare minerals. Sperrylite is platinum arsenide, $PtAs_2$, which is found in rare samples of the nickel-copper ores of Ontario and of copper ores at Rambler Mine, Laramie, Wyoming. Laurite is a rare ore composed mainly of ruthenium sulfide, RuS_2.

A few unusual nuggets have been discovered. The largest of these was found in 1843 in Russia and weighed 21.25 pounds. At war time prices this amount of pure platinum would be worth more than $36,000. A smaller nugget weighing 18⅓ pounds was found in Russia in 1834. The nuggets from South America are smaller, one of 800 grams being reported.[1]

Deposits of platinum are found widely distributed over the entire world.[2] Approximately 90 per cent of the total platinum produced has come from the alluvial deposits of Russia. Columbia ranks second, Borneo third, United States fourth, and Canada fifth. It is difficult to obtain accurate figures regarding the actual production in Russia because the published output was sometimes as much as 60 per cent below the actual production. This was to avoid registration. The total world's production up to 1917 has been variously estimated from 5,000,000 Troy ounces[3] to 11,000,000 ounces.[4] The price has gradually risen as the uses of these metals have increased. Table XLI shows the gradual rise during recent years. Owing to the scarcity of platinum during the war, and the urgent need for the metal, especially in munition work, the United States government set an arbitrary price of $105 per ounce, May, 1918. In June, 1923, prices in New York are quoted as follows: platinum $114.00 per ounce; iridium $260.00–$275.00; palladium $80.00.

Refining.[5] — All platinum ores have a high density varying from 14 to 19. Consequently the first steps in refining are usually made by a series of washings. Usually the ores are non-magnetic, but if the ore contains iron it may become highly

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[1] George F. Kunz, *Pan-American Union Bulletin*, Nov., 1917.

[2] See Platinum Map, p. 59, Monograph *The Platinum Metals*, by A. D. Lumb, British Imperial Institute (1920).

[3] J. M. Hill, *Eng. and Min. Jour.* **103** 1145 (1917).

[4] J. L. Howe, *Chem. and Met. Eng.* **19** 607 (1918).

[5] H. F. Keller, *Jour. Franklin Inst.*, Nov. (1912); *Les Métaux Précieux*, Jean Voisin (1922).

TABLE XLI

Prices of Platinum Metals in New York in Dollars per Troy Ounce

	PLATINUM[1]			IRIDIUM[2]	PALLADIUM[2]
	Low		High		
1910	28.00	——	39.25	——	——
1911	41.00	——	45.00	——	——
1912	——	45.00	——	——	——
1913	——	46.00	——	——	——
1914	43.00	——	48.00	65.00	44.00
1915	40.00	——	50.00	83.00	56.00
1916	60.00	——	110.00	94.00	67.00
1917	90.00	——	105.00	150.00	110.00
1918	——	108.00	——	175.00	135.00
1919	100.00	——	150.00	——	——
1920	85.00	——	155.00	——	——
1921	70.00	——	80.00	——	——
1922	85.00	——	87.50	165.00	55.00

magnetic. Separation by this property is somewhat uncertain, consequently gravity separation is generally used. If gold is present it is concentrated with the platinum and may be separated by repeated treatment with mercury. The crude platinum ore which remains is usually shipped without further treatment to the refiners.

Several methods are used in the refining of crude platinum ore, modifications being introduced to meet varying conditions, and usually the details of any process are closely guarded secrets. In general there are three steps used in the refining of the crude ore: (1) the removal of osmiridium, (2) the separation of platinum, and (3) the separation of the other metals which may be present. Two types of methods are used to accomplish these separations, known as the wet and dry methods. In the former the ore is digested under slightly increased pressure with aqua regia which contains an excess of hydrochloric acid. The undissolved residue consists mainly of osmiridium, sand, and graphite. The other metals are mainly brought into solution by this treatment. The solution is evaporated in the presence of excess HCl and the residue heated

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[1] Platinum figures are from *Min. Ind.* **29**, p. 547–548.

[2] Iridium and palladium values are from *Min. Resources*, 1918, p. 205.

to 150° to expel HNO_3 and convert palladium to the palladous condition. The residue is extracted with water, and the platinum is precipitated as ammonium platinichloride by adding a saturated solution of ammonium chloride. This is filtered, washed, and ignited, when spongy platinum is obtained. This is made into a paste, compressed, and hammered into bar form or melted in a lime furnace by an oxy-hydrogen flame or in an electric furnace. Prepared in this way the platinum usually contains about two per cent iridium, most of which may be removed by redissolving in aqua regia and repeating the ammonium chloride precipitation.

The dry process, sometimes called the method of Deville and Debray,[1] consists in heating the crude platinum ore with galena and litharge in a reverberatory furnace. Metallic lead is formed, which dissolves platinum, forming a fusible alloy. Iridosmine does not form an alloy with lead but settles to the bottom of the furnace and is removed. The alloy is cupeled, and the residual platinum may be purified by washing in nitric acid, dissolving in aqua regia and precipitating by NH_4Cl as in the wet method. Platinum prepared in this way contains iridium and rhodium and may contain other metals. The dry method gives uncertain results and is not extensively used.

Special methods are used for the reclaiming of platinum from other metallurgical processes. In the electrolytic refining of gold, the platinum metals are sometimes found in the slimes and sometimes they remain in the electrolyte. From the slimes the precious metals may be removed by the wet process and from the electrolyte by precipitation with NH_4Cl, after removal of gold with sulfur dioxide. The removal of platinum from the nickel-copper ores of Ontario is long and difficult. In the Orford process[2] the matte is fused with sodium sulfate and coke, then the "bottoms" roasted with salt and leached. Platinum is reclaimed from the mixed chloride-sulfate solution by an unpublished process. This method does not recover more than a small percentage of the precious metals.

A considerable amount of platinum is annually recovered from scrap metal, from electroplating solutions, and from waste in the manufacture of jewelry, in dentistry, and in photography.

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[1] *Ann. Chim. Phys.* **56** (1859); *ibid* **61** 5 (1861); *Compt. rend.* **81** 893 (1875).

[2] *Report Royal Ontario Nickel Commission* (1917), p. 454.

The methods employed in the recovery of platinum from such sources are varied [1] and naturally depend on the sort of material and the nature of the accompanying metals.

The production of chemically pure platinum is a difficult task, which involves the exclusion of the base metals and the elimination of the other members of the platinum group. The methods commonly employed for this purpose are similar to those used in the estimation of the metal.[2]

The other metals of the platinum group are obtained as by-products in the refining of platinum. The liquor obtained from the filtration of ammonium chlorplatinate may contain iridium, rhodium, palladium, and gold. The separation of these metals may be accomplished in several ways, the method shown in Table XLII being typical.[3]

The metals ruthenium, osmium, and iridium are conveniently recovered from the natural alloy called iridosmine or osmiridium. This is a white mineral, very hard, which contains mainly iridium (40 per cent) and osmium (17–48 per cent) with small amounts of ruthenium, rhodium, and platinum. In the refining of the platinum it is usually given separate treatment, such as that shown in Table XLIII.

Properties. *Ruthenium* in compact form resembles platinum in color and luster, but is somewhat harder and more brittle. Next to osmium, it is the most infusible metal of this group. It occludes gases readily, absorbing hydrogen when used as kathode in the electrolysis of water. In finely divided form the metal has a dull gray color and serves efficiently as a catalyst in such reactions as the oxidation of alcohol to aldehyde and acetic acid. Colloidal ruthenium is obtained by the action of reducing agents on aqueous solutions of ruthenium salts. Ruthenium sponge results from the ignition of ammonium chlor-ruthenate. Explosive ruthenium is prepared by dissolving its zinc alloy in hydrochloric acid. It is explosive even when prepared in the absence of air (compare rhodium and iridium). Bunsen's explanation of this behavior was the formation of an unstable

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[1] See *Recovering Precious Metals*, by G. E. Gee (Spon and Chamberlain, New York) and *The Precious Metals*, by T. K. Rose (Constable and Co., London).

[2] See article by Edward Wichers, *Jour. Am. Chem. Soc.* **43**, 1268 (1921).

[3] For other methods see Vaisin, *Les Métaux Précieux*, p. 130; Keller, *Jour. Franklin Inst.*, Nov., 1912.

Table XLII

The Separation of the Platinum Metals

<table>
<tr><td colspan="6">Crude ore is digested for several hours in aqua regia.</td></tr>
<tr><td rowspan="4">Residue: Contains iridosmine.</td><td colspan="5">Solution: Evaporate to a syrup, add HCl, and repeat several times. Take up with the least possible amount of water and add concentrated NH$_4$Cl. After standing filter.</td></tr>
<tr><td rowspan="3">Precipitate: Wash with NH$_4$Cl solution, dry and ignite: spongy platinum.</td><td colspan="4">Filtrate: Add zinc, filter the precipitated metals, wash with boiling water and add aqua regia.</td></tr>
<tr><td colspan="2">Residue: Boil with 10% KOH solution, wash, mix the residue with an equal weight of NaCl, and heat to 440° in an atmosphere of chlorine. Take up with water, crystallize the excess NaCl, heat the liquid with HNO$_3$ and add saturated NH$_4$Cl solution.</td><td colspan="2">Solution: Evaporate, take up with dilute HCl and add a solution of mercuric cyanide.</td></tr>
<tr><td>Precipitate: Wash and ignite: iridium.</td><td>Filtrate: Evaporate to crystallization and ignite the crystals: rhodium.</td><td>Precipitate: Wash and ignite: palladium.</td><td>Filtrate: Add a concentrated solution of ferrous sulfate. Filter and wash thoroughly with hot water: gold.</td></tr>
</table>

TABLE XLIII

Treatment of Iridosmine

<table>
<tr><td colspan="4">Fuse with excess of zinc as long as zinc fumes are expelled; pulverize and heat with BaO_2, then cool, add aqua regia, and distill one-fourth the volume.</td></tr>
<tr><td rowspan="3">Distillate: Contains osmic acid; redistill, collecting distillate in ammonia water, then add H_2S, precipitating OsS_4, which on heating in a closed crucible gives osmium.</td><td colspan="3">Undistilled liquor: Add H_2SO_4 and filter off $BaSO_4$; evaporate to dryness and remove silica; finally to the solution add a little aqua regia and then a strong solution of ammonium chloride.</td></tr>
<tr><td rowspan="2">Precipitate: Contains ammonium chloriridate with some platinum salt.</td><td colspan="2">Filtrate: Add metallic zinc, precipitating rhodium and ruthenium as a fine powder, which is fused with KOH and KNO_3 and the melt extracted with water.</td></tr>
<tr><td>Insoluble Portion: Contains rhodium.</td><td>Soluble Portion: Contains potassium ruthenate; add HNO_3, precipitating ruthenium oxide, which on ignition yields ruthenium.</td></tr>
</table>

allotropic modification, which reverts to a stable form with the liberation of much heat.

Ruthenium occludes oxygen when the metal is melted in the air and at the same time it is covered with a thin film of the oxide. When heated in oxygen it forms the brown oxide RuO_2 and at temperatures above 600° some RuO_4 is formed. It unites with oxygen most readily of the platinum metals except osmium. Fluorine and chlorine combine directly with ruthenium at somewhat elevated temperatures. The metal is not attacked by any single acid and aqua regia dissolves it slowly. Fused acid sulfates have no effect upon ruthenium, the best solvent being a mixture of potassium hydroxide and potassium nitrate, the ruthenate K_2RuO_4 being formed. The metal may also be brought into solution by fusion with sodium peroxide. The finely divided metal is quite readily soluble in alkali hypochlorite solutions.

Rhodium resembles aluminium in appearance; it is ductile and malleable at red heat; is less fusible than platinum, but the molten metal spits on cooling. When alloyed with platinum it reduces the volatility of the latter. Molten rhodium dissolves considerable carbon, but on cooling, the carbon appears again as graphite. Finely divided rhodium is formed by reduction of its salts in hydrogen; it absorbs hydrogen only slightly but catalyzes the union of hydrogen and oxygen. Rhodium may be prepared in both colloidal and explosive forms like ruthenium, except that explosive rhodium must be prepared in the presence of air. The spongy metal does not absorb gas. Rhodium black is prepared by reduction of rhodium salts in alkaline solution with alcohol or ammonium formate. The presence of sulfur compounds appears to be necessary. It is a powerful catalyst, oxidizing formic acid at ordinary temperatures. It forms a fusible and extremely malleable alloy with silver; it alloys readily with copper, bismuth, tin, lead, zinc, and platinum.

When heated in the air rhodium tarnishes very slightly, but it is the most readily attacked of all the platinum metals by chlorine and bromine, the action on finely divided metal beginning at 250°. The pure metal is insoluble in acids and aqua regia, but when alloyed with small amounts of other metals, especially copper, lead or zinc, it is much more easily soluble. In the presence of oxygen, hydrochloric acid under pressure attacks the metal at a temperature of 150°. Fused potassium acid sulfate dissolves rhodium, forming a double sulfate, and fused nitrate yields the sesquioxide.

Palladium is a white metal, somewhat harder than platinum, possessing somewhat less ductility and malleability. When heated it softens at temperatures below its melting point, consequently it may be welded readily. Its melting point, about 1542°, is the lowest of the platinum metals, but it vaporizes below the melting point, producing green vapors. Its boiling point is approximately 2540°.

Colloidal palladium is prepared by reduction of the chloride with acrolein or hydrazine hydrate in the presence of a protective colloid. The colloidal particles are extremely small. It catalyzes the liberation of oxygen from hydrogen peroxide in the presence of an alkali, but not in acid solution. As little as a milligram of colloidal palladium in 2,500 liters of solution may be detected[1] by the use of NaOH and H_2O_2. Colloidal palladium has remarkable power of absorbing gases. The amount of hydrogen absorbed by a single sample has been observed[2] to vary between 926 and 2,952 volumes. Not all of the hydrogen is expelled when the solution is heated, but the activity of hydrogen is increased by absorption in colloidal palladium. Acetylene is also absorbed rapidly at first, then more slowly, the reaction continuing for several days. Nearly 5,000 volumes may finally be occluded by increased temperature and pressure, only part of which is given up when the solution is exposed to the air.

Palladium sponge is best obtained by heating $(NH_4)_2PdCl_4$ or $(NH_4)_2PdCl_6$, in hydrogen. The metal in this form absorbs hydrogen readily, the amount taken up depending on temperature. At 20° the occluding power reaches a maximum, when 861 volumes are taken up; at 105°, 751 volumes are absorbed, at − 50, 917 volumes, and at the temperature of liquid air the amount of hydrogen absorbed is so great that palladium sponge is useful in removing the last traces of hydrogen from other gases.[3]

Palladium black is prepared by reducing the solutions of palladium salts by such reducing agents as sodium formate. It is not the pure metal, but it contains some oxide, as much as 12 per cent. PdO being found. When palladium black is heated in hydrogen, the gas is readily absorbed with material evolution of heat. At higher temperatures the hydrogen is set free, as much as 674 volumes of gas being evolved by one volume of metal. When palladium black is suspended in water, its power of absorbing hydrogen is increased until it has been known[4] to absorb 1,204 volumes of the gas. It also absorbs acetylene, whose chemical activity is increased by this process. Palladium black absorbs carbon monoxide, 36 volumes being taken up slowly at ordinary temperatures; this gas is rapidly expelled when heated to 520° C.

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[1] Bredig and Fortner, *Ber.* **37** 798 (1904).
[2] Paal and Gerum, *ibid.* **41** 805 (1908).
[3] Valentiner, *Ber. Deut. physikal. Ges.* **13** 1003 (1911).
[4] Paal and Gerum, *Ber.* **41** 818 (1908).

Palladium is not tarnished in dry or moist air or in ozone at ordinary temperatures. At dull redness it unites with oxygen, giving PdO. When the molten metal solidifies, it "spits" like silver. All of the halogens attack palladium at elevated temperature, though iodine vapor reacts only incompletely with the finely divided metal. Sulfur and arsenic unite directly with the metal at elevated temperatures. Hydrochloric acid dissolves the compact metal slowly, but aqua regia is a good solvent. Concentrated nitric acid attacks the metal, while dilute nitric acid will dissolve certain alloys but not the pure metal. Sulfuric acid, hot and concentrated, forms $PdSO_4$, which is also formed by fusion with $KHSO_4$. Palladium is sufficiently active to displace mercury from the cyanide.

Osmium in crystalline form, obtained by treating its zinc alloy with HCl, has a bluish tint, is brittle, hard enough to scratch glass, and has the highest density of any known substance. Its melting point is the highest of the members of this group, and it vaporizes slowly. Colloidal osmium is prepared by reducing potassium osmate, K_2OsO_4, and is effective in catalyzing the hydrogenation of unsaturated compounds and in the oxidation of carbon monoxide. It is the most effective of all the colloidal metals of this group in catalyzing the decomposition of hydrogen peroxide. The most marked catalytic effect of the metal is in the finely divided form, in which condition it causes the union of hydrogen and oxygen to become explosive at temperatures as low as 40° or 50° C. It is one of the most effective catalysts in the Haber process.[1]

Osmium is the only metal of this group which unites readily with oxygen. The finely divided metal reacts with oxygen of air at ordinary temperatures, this reaction probably being catalyzed by the presence of absorbed hydrogen. It is also oxidized by steam. The product of oxidation, OsO_4, has a disagreeable odor, from which the element received its name. These vapors are poisonous and produce temporary blindness.[2] None of the halogens attack the metal at ordinary temperatures, but both fluorine and chlorine unite with it when heated. The amorphous metal dissolves readily in fuming nitric acid and less readily in aqua regia; acids do not attack the crystalline form,

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[1] *Zeit. Elektrochem.* **19** 53 (1913).

[2] Deville and Debray, *Ann. Chim. Phys.* **56** 385 (1859).

but the metal is easily brought into solution by fusion with a mixture of sodium peroxide and nitrate or of the corresponding barium salts. Finely divided osmium is soluble in alkali hypochlorite solutions, thus illustrating its acidic tendency.

Iridium. The fused metal is white, with a bluish luster, resembling polished steel in appearance. As usually obtained it is hard, brittle, and almost entirely lacking in ductility. It is now believed that its hardness and brittleness are due to impurities and that the pure metal is quite malleable. It has been both melted and vaporized [1] in the electric furnace. The molten metal absorbs carbon, which reappears as graphite when the metal solidifies. Iridium foil may be made to absorb considerable hydrogen, when it actively catalyzes the union of hydrogen and oxygen. *Explosive iridium* is made by preparing a zinc alloy of the metal and then removing the zinc with hydrochloric acid. The finely divided metal which remains is explosive, if the process has been carried out in the air. *Colloidal iridium* is made by reducing a solution of the chloride with various reducing agents in the presence of a protective colloid. The color varies from red to black, depending on the method of preparation. As a catalyst it is less active than platinum, but it aids in the decomposition of hydrogen peroxide, best in the presence of dilute acids; it also causes the union of carbon monoxide and oxygen at ordinary temperatures. *Iridium black* is conveniently prepared by dissolving the sesquioxide in an alkaline solution and then adding alcohol and boiling. The fine black precipitate obtained in this way is a mixture of the metal and its oxides. It is an active catalyst.

In the finely divided state, iridium shows some chemical activity. At a red heat it begins to unite slowly with the oxygen of the air, with sulfur vapor, or phosphorus. The phosphide,[2] Ir_2P, is decomposed at higher temperatures and the sulfide, Ir_2S, may likewise be prepared by passing hydrogen sulfide over ammonium chloriridate. If hydrogen selenide is used, Ir_2Se is formed. The compact metal is much less active, but at 1100° a superficial oxidation begins, forming a purple layer. Fluorine in the nascent state and at dull red temperatures forms a fluoride, and chlorine attacks the hot metal, especially in the presence

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[1] Moissan, *Compt. rend.* **142** 189 (1906).

[2] Clark and Joslin, *Am. Chem. Jour.* **5** 231 (1883).

of sodium chloride, forming a soluble double salt. All simple acids and even aqua regia are without action on the metal except in very finely divided state or in alloys, in which condition a slow partial solution may take place. Fused alkalies in the presence of alkaline nitrates form soluble and insoluble iridates, and potassium bisulfate forms the insoluble oxide.

Platinum is a white metal, intermediate in color between silver and tin. It is softer than most of the other metals of this group and in both malleability and ductility it approaches silver and gold. Its electrical conductivity is low, and its coefficient of expansion is the lowest of all metals. The hardness is increased by the addition of iridium, but the ductility is at the same time decreased. The hardness of the metal is increased also by mechanical working and decreased by keeping for a time at a bright red heat. The volatility of platinum at temperatures below its melting point has been carefully studied. It has been shown[1] that it is much more volatile in the presence of oxygen than it is in hydrogen, nitrogen, or a vacuum. In oxygen the "vaporization" begins at a temperature as low as 500° C., when it is supposed that an endothermic oxide, PtO_2, is formed which dissociates at lower temperatures. The loss of platinum by volatilization at temperatures above 900° is increased by the presence of iridium but decreased by rhodium.[2] Heated platinum foil permits hydrogen to diffuse but not methane, nitrogen, oxygen, helium, or argon. The compact metal absorbs some hydrogen, but it is all given up on cooling.

Finely divided platinum is an active catalyst, and may be conveniently prepared on asbestos fiber by dipping the fiber in a solution of chlorplatinic acid and igniting. Platinized nickel is made by shaking the powdered metal with a solution of chlorplatinic acid. The catalytic activity of platinum is not affected by nickel, but it is decreased or entirely destroyed by certain other metals.

Colloidal platinum is prepared by reduction of the chloride in the presence of a protective colloid or by passing a spark between platinum electrodes in ice water. It catalyzes the decomposition of hydrogen peroxide in both acid and alkaline solution; the union of oxygen with both carbon monoxide and with

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[1] Roberts, *Phil. Mag.* **25** 270 (1913).

[2] Burgess and Sale, *Bureau of Standards, Scientific Paper* No. 254 (1915).

hydrogen; the hydrogenation of unsaturated oils; and the reduction of many organic substances.

Platinum black is produced by the reduction of solutions with reducing agents such as alcohol, sodium formate, or hydrazine hydrate, all in the presence of an alkali. Sheets of metallic aluminium are especially serviceable for this purpose, since a pure finely divided precipitate is obtained. It absorbs both hydrogen and oxygen, and there is reason to believe that platinous hydroxide is formed. It is a powerful catalyst, effecting both oxidation and reduction reactions. It causes hydrogen and oxygen to combine explosively, but does not aid the union of carbon monoxide and oxygen. In the presence of glucose it reduces nitric acid to ammonia, potassium chlorate or perchlorate to the chloride, and potassium iodate to the iodide.[1] Platinum black will absorb 60 volumes of carbon monoxide but gives it up rapidly at 250°.

Platinum sponge is a soft porous mass, slate gray in color; it is prepared by heating ammonium chlorplatinate. It absorbs hydrogen readily, and if it is exposed to the air after taking up hydrogen it aids the union of hydrogen and oxygen so much that it begins to glow. Döbereiner made use of this property for the preparation of a self-lighting gas lamp. Platinum sponge also catalyzes the union of hydrogen and the halogens.

Explosive platinum is prepared by dissolving platinum in an excess of molten zinc, then removing the zinc with acid. This form of the metal must be prepared in the presence of oxygen, but the explosive nature of the product is less certain than in the case of the other metals of this group.

Platinum remains untarnished when heated in the air, and in this respect it is one of the most permanent of the metals. When platinum sponge or foil is heated in dry oxygen there is formed a thin layer of a black oxide, PtO, which is decomposed at higher temperatures. When the molten metal is cooled rapidly it "spits" in the manner characteristic of silver.[2] The compact metal is attacked by fluorine above 500° and by chlorine at about 1400°. The pure metal is not attacked by either hydrochloric or nitric acid alone, but aqua regia is a good solvent,

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[1] *Jour. Chem. Soc.* **90** (2), 862 (1906).

[2] Some authors claim that spitting occurs when platinum is heated in oxygen; others say this phenomenon is displayed when the metal is heated in reducing gases, but not when heated in an oxidizing flame or an electric induction furnace.

also a mixture of hydrochloric and chloric acids. Dilute
ic acid does not attack platinum, but the hot concen-
l acid attacks it slowly, forming such compounds as
H) $\cdot (HSO_4)_2$. Fused alkali carbonates have little effect
platinum, fused nitrates and acid sulfates are more
, while the fused hydroxides and peroxides attack it
. Sulfur does not attack platinum, but some of the
lic sulfides do. Phosphorus reacts easily with platinum,
ng a series of fusible compounds such as PtP_2, PtP, Pt_2P,
t_3P_5.[1] Hence phosphates or phosphides should never be
d in platinum under reducing conditions. Arsenic and
n also combine readily with platinum.

es. — *Ruthenium* has no commercial uses at present. Its
eness and ease of oxidation are decided disadvantages in
e as a metal.

odium is used to a moderate degree as an alloy of platinum.
most important effect of a small per cent of rhodium is
crease the volatility of the platinum. Consequently, an
containing 10 per cent rhodium is sometimes used for
ng laboratory dishes, and it is the most successful material
se as the positive element of the precious metal thermo-
e. Rhodium is also used in alloys with platinum for
ry.

lladium is used widely as a catalyst and in gas analysis; its
s with gold are used as platinum substitutes, not only in
nanufacture of various types of scientific equipment but
in dentistry, jewelry, and for plated ware.

mium was the first metal which was found to be commer-
successful in an incandescent electric bulb. Such fila-
s were expensive not only because of the scarcity of the
l, but also because of the difficulty of extraction and danger
its poisonous fumes. Such filaments were quickly replaced
hers which were more efficient and less expensive. In the
r divided forms it is active as a catalyst, and would be used
isively in such reactions as the Haber process if it could be
ned in sufficient quantities at a reasonable price. Its use
e form of " osmic acid " as a stain for fatty tissues is well
n. Osmium finds some use as an alloy in platinum jewelry,
ts presence is generally considered to be undesirable.

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[1] Clark and Joslin, *Am. Chem. Jour.* **5** 231 (1883).

Iridium is little used as a pure metal on account of its brittleness and the fact that it is less common than platinum. It is the most common alloy in platinum, whose ductility and malleability are decreased and whose volatility at lower temperatures is increased by the presence of iridium. Formerly platinum ware almost invariably contained at least 2 per cent iridium, but modern ware usually contains less than 2 per cent. If the alloy does not contain more than 10 per cent, it is readily worked. Platinum electrical equipment may contain from 10 to 30 per cent iridium. On account of their resistance to corrosion platinum-iridium alloys are highly prized for making chemical utensils and standard weights. Because of its low coefficient of expansion as well as its permanence, a similar alloy is used for making standard units of length. Surgical instruments, jewelry, contact points, and the points of fountain pens sometimes are iridium alloys. Its oxide is used in china painting and its salts in photography.

Platinum is widely used[1] for making chemical apparatus, in various scientific instruments, in electrical appliances, dentistry, jewelry, and as catalyst in a great variety of industries. During the recent war the importance of platinum as a catalyst became very vital, especially in the contact process for sulfuric acid and in the oxidation of NH_3 to HNO_3. Platinum salts are used in photography for the production of pleasing and permanent prints; the double barium platinum cyanide is especially useful in X-ray photography as a coating for the fluorescing screen. Platinum is by far the most important metal of the group.

Hard platinum is a name applied to the metal which has been hardened by alloying with other metals, usually iridium or palladium. Recently laws have been passed[2] in some of the states specifying that hard platinum offered for sale or manufacture must contain 925 parts per thousand platinum, and may be alloyed only with the other metals of the platinum group. Hard platinum is much used in jewelry and dentistry.

Compounds. The compounds formed by the metals of the Platinum Group show both striking resemblances and surprising contrasts. Since platinum is by far the most familiar member of the group, its compounds are most important. Conse-

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[1] See *Les Métaux Précieux*, Jean [illegible], pp. 206, 236.

[2] Criminal Code of Illinois, Section 225a, 1921. New York has a similar law.

quently, the platinum compounds are discussed somewhat fully and the more important compounds of the other metals are grouped in tabular form.

Platinum forms two series of salts, the platinous, in which the metal is bivalent, and the platinic, which are quadrivalent. Both classes of compounds are decomposed by heat, and the metal is easily displaced from platinic solutions by most other metals and many organic substances. There is a marked tendency to form complex compounds.

Oxygen combines directly with platinum sponge or thin foil, a part of which reacts to form PtO. This compound is soluble in acids, giving platinous salts, and is decomposed by heat, yielding PtO_2 and the metal.

Hydrated platinum monoxide, $PtO \cdot 2H_2O$, is obtained by adding a fixed alkali to a warm solution of platinous chloride or potassium chloroplatinite. It is easily oxidized, and when freshly precipitated it is quite readily soluble in concentrated acids. After it has been dried in an atmosphere of carbon dioxide it becomes almost insoluble in acids except hydrochloric.

Platinum sesquioxide has not been prepared in the anhydrous state, but a brown precipitate $Pt_2O_3 \cdot xH_2O$ is obtained when hot sodium carbonate solution is added to platinous chloride.

Platinum dioxide is obtained as a monohydrate of the formula $PtO_2 \cdot H_2O$ in the following manner: a solution of platinic tetrachloride is boiled with an excess of NaOH and then neutralized with acetic acid; the precipitate so obtained is dried thoroughly at 100°; this substance loses water with difficulty and on strong ignition yields metallic platinum, but it is difficult to expel all the oxygen.[1] Higher hydrates of PtO_2 are obtainable, a white tetrahydrate being obtained when the platinic chloride is quite dilute and the acetic acid is cold. This compound has acidic properties and is sometimes called hexahydroplatinic acid, to which the formula $H_2Pt(OH)_6$ is assigned. It dissolves in dilute caustic alkali solutions, forming such salts as potassium hexahydroxyplatinate, $K_2Pt(OH)_6$, which behaves like a salt of a dibasic acid.

Platinum trioxide, PtO_3, is obtained[2] at the anode when a solution of potassium hexahydroplatinate is electrolyzed, using platinum electrodes. Its formation may possibly account for the anodic passivity of platinum. It is readily soluble in hydrochloric acid, but difficultly soluble in nitric and sulfuric acids. Wohler considers it as the anhydride of platinic acid and not as a peroxide.

Fluorine combines directly with platinum at 500° to 600°, forming both PtF_2 and PtF_4. Efforts to prepare fluorine compounds of platinum by indirect means have been unsuccessful.[3]

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[1] Wöhler and Frey, *Zeit. für Electrochem.* **15** 129 (1909).

[2] Wöhler and Martin, *Ber.* **42** 3326 (1909).

[3] Ruff and others, *Ber.* **46** 920 (1913).

Chlorine forms $PtCl_2$, $PtCl_3$, and $PtCl_4$, and a large number of complex salts.

Platinum dichloride or platinous chloride is obtained by heating platinum black in chlorine at 360° or by heating chlorplatinous acid, H_2PtCl_4, at 100°. It is insoluble in water, but soluble in HCl, forming tetrachlorplatinous acid, H_2PtCl_4. Salts of this acid are important and are quite stable. They are prepared by reduction of the corresponding chlorplatinates, best by potassium oxalate: $M_2PtCl_6 + K_2C_2O_4 = M_2PtCl_4 + 2\,KCl + 2\,CO_2$. The chlorplatinites are generally soluble in water, yielding red solutions, but the silver, lead, mercury, and thallium salts are difficultly soluble.

Platinum trichloride is prepared by heating $PtCl_4$ in dry chlorine at 390°. It is readily soluble in boiling water, but may be hydrolyzed by continued boiling. The trichloride does not dissolve in concentrated HCl, but when the mixture is warmed a reaction takes place, producing both $PtCl_2$ and $PtCl_4$.

Platinum tetrachloride or platinic chloride, $PtCl_4$, may be prepared by heating chlorplatinic acid in a stream of HCl or chlorine. It has a reddish brown color, and on exposure to air it absorbs moisture, becoming bright yellow in color. It dissolves fairly well in warm water, the solution being strongly acidic, as is shown by the fact that it liberates carbon dioxide from the carbonates. The solution is reduced by iodine, thus: $PtCl_4 + I_2 = PtCl_2 + 2\,ICl$, a reaction used for the volumetric estimation of platinum.

Hexachlorplatinic acid, H_2PtCl_6, is prepared by dissolving platinum in aqua regia or a mixture of chloric and concentrated hydrochloric acids; or by dissolving platinum sponge in hydrochloric acid in the presence of chlorine; or by dissolving platinum black in a mixture of concentrated HCl and H_2O_2; or by the anodic oxidation of platinum sponge or black. If the solution is evaporated crystals of $H_2PtCl_6 \cdot 6\,H_2O$ are obtained. The solution is a fairly strong acid, decomposing carbonates and neutralizing bases, forming chlorplatinates of the general formula M_2PtCl_6. Of these the most important are $(NH_4)_2PtCl_6$ and K_2PtCl_6. They resemble each other in appearance, both are difficultly soluble in water, and they are isomorphous. The former is important in the purification of platinum and in the preparation of platinum sponge; the latter is used in the quantitative determination of both platinum and potassium.

Bromine and *iodine* form compounds PtX_2, PtX_4, and H_2PtX_6, analogous to the corresponding chlorine compounds.

Sulfur combines with platinum sponge or the finely divided metal on ignition and forms PtS. The same product is also produced when hydrogen sulfide is passed into a solution of an alkali chlorplatinite.

Platinum disulfide, PtS_2, is precipitated when hydrogen sulfide is passed into a hot solution of $PtCl_4$. It is a black powder which on exposure to the air forms an oxysulfide, $PtOS \cdot xH_2O$, but on heating strongly in the air the sulfur burns, leaving the metal. The disulfide dissolves only slightly in both acids and alkali sulfides.

Platinic sulfate, $Pt(SO_4)_2$, is formed by the slow solution of platinum sponge in concentrated sulfuric acid. Basic sulfates are also prepared by dissolving hydrated platinum dioxide in sulfuric acid.

Selenium combines directly with platinum, forming PtSe, a very brittle substance. By reduction of an alkali chlorplatinate in the presence of a selenite a compound of the formula $PtSe_3$ is obtained.

Tellurium combines with finely divided platinum, yielding $PtTe_2$, which on heating yields both PtTe and Pt_2Te.

Phosphorus reacts readily with platinum, forming a fusible mass which probably contains a mixture of compounds such as PtP_2, PtP, Pt_2P, and Pt_3P_5.

Arsenic combines with platinum sponge at elevated temperatures, forming $PtAs_2$, which is found in nature as the mineral sperrylite.

Antimony powder when mixed with platinum sponge and heated gives $PtSb_2$, PtSb, and Pt_5Sb_2.

Silicon unites with platinum when the two elements are heated together, PtSi being formed at moderate temperatures and Pt_2Si in the electric furnace.

Carbonyl compounds are formed with platinous derivatives, as, for example, by passing carbon monoxide over platinous chloride at 250°. Under these conditions there is obtained a mixture of $PtCl \cdot 2\,CO$, and $2\,PtCl_2 \cdot 3\,CO$, which on further heating gives $PtCl_2 \cdot CO$. Other platinous compounds yield similar derivatives. Carbonyl compounds may also be prepared by passing an equimolecular mixture of carbon monoxide and chlorine over platinum sponge or foil at 240°-250°. This reaction is sometimes used to detect the presence of small amounts of rhodium or certain base metals in platinum.[1]

Cyanogen derivatives are numerous and capable of great complexity. Platinous cyanide $Pt(CN)_2$, is obtained as a yellow precipitate when mercuric cyanide is added to a solution of alkali chlorplatinite. Double cyanides of the general formula $M'_2Pt(CN)_4$ are formed by such reactions as $6\,KCN + PtCl_4 = K_2Pt(CN)_4 + 4\,KCl + (CN)_2$. These platinocyanides do not respond to the ordinary tests for platinum. These compounds yield beautifully colored hydrates, and the barium and calcium hydrates have optical isomeric modifications.[2] Certain of these hydrates become remarkably fluorescent under excitation from ultraviolet light or radium.

Ammonia added to solutions of platinum salts produces a large series of complex derivatives, which are analogous to the compounds of chromium and cobalt, obtained in a similar manner. These salts do not give the ordinary reactions for platinum, but are capable of undergoing various decompositions, thus furnishing a large number of derivatives. Many cases of isomerism occur among these compounds, which have been extensively studied by Werner.[3] According to his system, the compounds are classified on the theory of principal and supplementary valence. The principal valence is that shown by an atom or radical which can exist as an ion, while

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[1] Mylius and Foerster, *Ber.* **25** 665 (1892).

[2] Levy, *Trans. Chem. Soc.* **89** 125 (1906); **93** 1446 (1908); **101** 1081 (1912).

[3] A. Werner, *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie*, or the translation in English by Edgar P. Hadley, *New Ideas on Inorganic Chemistry*.

the supplementary valence is that displayed by radicals which cannot exist as ions. Thus an atom of platinum can hold four chlorine atoms by means of the principal valences, giving the molecule $PtCl_4$. But this molecule can combine with two molecules of hydrochloric acid by means of the secondary valences of platinum and chlorine, giving H_2PtCl_6.

Platinum forms two distinct series of these complex salts, in one of which platinum is bivalent and in the other quadrivalent. In the platinous series the metal holds four molecules or radicals coördinated with it to form the complex radical, which in turn may hold two external radicals. Thus when ammonia is added to platinous chloride and the precipitate so formed is boiled with ammonia, a compound is formed having the composition $[(NH_3)_4Pt]Cl_2$. The ammonia groups may be partially or entirely replaced by acid groups such as Cl, NO_2, SCN, etc. Thus we have four classes of derivatives which correspond to the following general formulae, X being used to represent any univalent acid radical and R any univalent basic radical.

1. $[(NH_3)_4Pt]X_2$, Tetrammine platinous compounds.
2. $[X(NH_3)_3Pt]X$, Triammine platinous compounds.
3. $[X_2(NH_3)_2Pt]$, Diammine platinous compounds.
4. $[X_3(NH_3)Pt]R$, Monammine platinous compounds.

Platinic derivatives of a similar nature are formed by oxidizing the platinum in any of the platinous derivatives. With the metal in the quadrivalent state, the complex is capable of holding six molecules or radicals, while a maximum of four external acid radicals may attach to the complex as a whole. Thus we have the following series of platinic complexes: —

1. $[(NH_3)_6Pt]X_4$, Hexammine platinic compounds.
2. $[X_2(NH_3)_4Pt]X_2$, Tetrammine platinic compounds.
3. $[X_3(NH_3)_3Pt]X$, Triammine platinic compounds.
4. $[X_4(NH_3)_2Pt]$, Diammine platinic compounds.
5. $[X_5(NH_3)Pt]R$, Monammine platinic compounds.

To make the group complete there should be a pentammine series, but derivatives of this type are not known.

In addition to these series of derivatives others are known in which the ammonia radical is replaced by substituted ammonias. A few derivatives which contain more than one atom of platinum have also been prepared. These suggest enormous possibilities in the study of the complex compounds of platinum.

The other platinum metals form compounds which are in general similar to those formed by platinum. Table XLIV gives in tabular form the principal compounds formed by the associated metals. In general their formation, characteristics, and properties will be suggested by comparison with the corresponding platinum derivatives. The following characteristics are worthy of note.

Ruthenium is basic in the lower states of oxidation, while its higher oxides are acidic. A trioxide, RuO_3, and heptoxide are known only in combination.

TABLE XLIV

Typical Compounds[1] *of the Platinum Group Metals.*

	Ru	Rh	Pd	Os	Ir
Oxides . . .	—	—	PdO	OsO	—
	Ru_2O_3	Rh_2O_3	$Pd_2O_3 \cdot xH_2O$	Os_2O_3	Ir_2O_3
	RuO_2	RhO_2	$PdO_2 \cdot xH_2O$	OsO_2	IrO_2
	—	RhO_3	—	—	IrO_3
	RuO_4	—	—	OsO_4	—
Salts -ite . .	M'_2RuO_3	—	—	Osmyl $M_2OsO_2X_4$	—
-ate . .	M'_2RuO_4	M'_2RhO_4	—	M_2OsO_4	—
Per -ate . .	M'_2RuO_4	—	—	—	—
Chlorides . . .	—	—	—	—	IrCl
	$RuCl_2$	$RhCl_2$	$PdCl_2$	$OsCl_2$	$IrCl_2$
	$RuCl_3$	$RhCl_3$	$PdCl_3$	$OsCl_3$	$IrCl_3$
	$RuCl_4$	—	—	$OsCl_4$	$IrCl_4$
Chloro-salts -ite	M'_3RuCl_6	M'_3RhCl_6 M'_3RhCl_6	M'_2PdCl_4	M'_3OsCl_6	M'_3IrCl_6
-ate	—	—	M'_2PdCl_6	M'_2OsCl_6	M'_2IrCl_6
Sulfides . . .	—	—	Pd_2S	—	—
	—	RhS	PdS	—	IrS(?)
	Ru_2S_3	Rh_2S_3	—	—	Ir_2S_3
	RuS_2	—	PdS_2	OsS_2	IrS_2
	RuS_3	—	—	—	
				OsS_4	
Sulfites . . .	—	—	—	$OsSO_3$	—
	$Ru_2(SO_3)_3$	$Rh_2(SO_3)_3$	—	—	$Ir_2(SO_3)_3$
Sulfates . . .	—	—	$PdSO_4$	—	—
	—	$Rh_2(SO_4)_3$	—	—	$Ir_2(SO_4)_3$
	$Ru(SO_4)_2$	—	—	—	—
Nitrates . . .	—	$Rh(NO_3)_3$	$Pd(NO_3)_2$	—	—
Cyanides . . .	—	$Rh(CN)_3$	$Pd(CN)_2$	$Os(CN)_2$	$Ir(CN)_3$
	$K_4Ru(CN)_6$	$K_3Rh(CN)_6$	$K_2Pd(CN)_4$	$K_4Os(CN)_6$	$K_3Ir(CN)_6$

The tetroxide, RuO_4, is volatile with an odor resembling ozone, but it is not poisonous. It is soluble in alkalies, and the perruthenate so formed is useful in histology as a stain because of the ease with which it is reduced by organic substances, giving the finely divided metal.

Rhodium is almost wholly basic in character, its salts being generally trivalent. The trichloride forms double salts with alkali chlorides which are called hexachlorrhodites, M'_3RhCl_6, and pentachlorrhodites, M_2RHCl_5, respectively. These may be considered as double chlorides rather than as salts of the respective chloro-acids, since the existence of the latter is doubtful. The trichloride is insoluble in water and acids, but its hydrate is soluble.

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[1] Compounds of doubtful existence and those known only in complexes are not included in this table.

Rhodium and sulfur combine with incandescence at a definite temperature forming RhS. The sesquisulfide is known in two modifications: the one, produced by heating dry $RhCl_3$ in H_2S at 360°, and the other formed by precipitating $RhCl_3$ solution with H_2S. A sesquisulfate is formed by dissolving Rh_2O_3 in sulfuric acid, and this salt readily forms alums with the alkali metals.

With ammonia rhodium forms several series of complex salts which resemble the cobalt salts. The three principal series are as follows, X being a univalent negative element or radical:

$[Rh(NH_3)_6]X_3$, Hexammine salts
$[Rh(H_2O)(NH_3)_5]X_3$, Aquopentammine salts
$[RhX(NH_3)_5]X_2$, Pentammine salts

Palladium compounds resemble those formed by platinum more closely than any other member of the group. It forms two series of salts, the palladous, in which the metal is bivalent, and the palladic, which are generally quadrivalent. The former are more numerous and more stable, though the quadrivalent salts form numerous double salts, some of which are stable. Palladous salts are easily oxidized to palladic compounds, which in turn are efficient oxidizing agents. Palladium forms double nitrites and cyanides which resemble the corresponding compounds of cobalt and nickel. The double palladium nitrites are much more soluble than the analogous compounds of cobalt. The salts of palladium easily yield the metal under the influence of reducing agents and heat.

Ammonia reacts with palladous salts producing two series of salts, whose general formulas are as follows, X being any negative element or radical:

$[Pd(NH_3)_2X_2]$, Palladosammine salts
$[Pd(NH_3)_4]X_2$, Palladodiammine salts

Osmium compounds display five degrees of oxidation. In the bivalent and trivalent conditions the metal is rather basic in character, only a few compounds being known. $OsCl_4$ is stable enough to permit it to be sublimed and it forms important double salts, the hexachlorosmates. The hexavalent oxide, OsO_3, is unknown and its acid, H_2OsO_4, correctly called osmic acid, is doubtful. But the osmates, like K_2OsO_4, may be prepared by fusing the metal with KNO_3 and KOH.

The highest oxide, OsO_4, is probably the best known and most important compound of osmium. It is erroneously called osmic acid. It may be made by heating osmium in the air or in nitric acid. It is volatile, yielding an ill-smelling vapor which is irritating and poisonous, producing temporary blindness. The best antidote is the inhaling of hydrogen sulfide. It is soluble in water, alcohol, and ether, the solution being used as a stain for fat and nerve tissue. The oxide is used as a catalyst in both oxidation and reduction reactions, as in the oxidation of arsenic by $KClO_3$, and in the hydrogenation of unsaturated oils.

The osmyl derivatives, such as potassium osmyl nitrite, $K_2(OsO_2(NO_2)_4)$, may be prepared by the action of a reducing agent on OsO_4 in the presence of a salt, thus: $OsO_4 + 2\,NO + 2\,KNO_2 = K_2(OsO_2(NO_2)_4)$.

Osmiamic acid, $OsNO_3H$, is prepared by adding dilute sulfuric acid to the barium salt or hydrochloric acid to the silver salt. The acid is unknown except in dilute water solution. Its potassium salt is obtained as unstable orange-yellow crystals when ammonia is added to a cold solution of OsO_4 in KOH, thus: $OsO_4 + KOH + NH_3 = OsNO_3K + 2\ H_2O$. The barium and silver salts are prepared in a similar manner.

Iridium forms three series of simple salts in which the metal has valence of two, three, and four. The lower oxide, IrO, has been reported, but is doubtless unknown in the pure state.[1] Salts of this state of valence are not numerous or well known. On ignition of iridious chloride, $IrCl_2$, in chlorine a monochloride is formed,[2] but it is only stable between 773° and 798° C.

In most of its compounds iridium is either trivalent or quadrivalent, the latter being called iridic. In both states of valence, the halogen compounds form double salts with the corresponding alkali halides, giving chloriridites and chloriridates respectively. These are to be considered as alkali salts of complex acids.

In its trivalent form, iridium forms the sesquisulfate, $Ir_2(SO_4)_3$, which like the corresponding salts of cobalt and rhodium forms a series of alums.

Double cyanides are formed such as potassium iridiocyanide, $K_4Ir''(CN)_6$, similar to ferrocyanide; and potassium iridicyanide, $K_3Ir'''(CN''')_6$ to ferricyanide. The latter is more stable.

Ammonia forms complex derivatives with all three classes of iridium compounds. When added to iridious chloride, $IrCl_2$, or to iridic chloride, $IrCl_4$, the complex salts formed are analogous to the series of platinous and platinic ammine derivatives. When ammonia is added to the trichloride, many complex derivatives are formed which are similar to rhodic, cobaltic, and chromic compounds. For example, when ammonia acts upon ammonium iridiochloride a compound is produced having the formula $[Cl(NH_3)_5Ir]Cl_2$, and called chloro-pentammine-iridium dichloride.

Detection. — The qualitative separation of the metals of the platinum group is a difficult task, for which many methods have been proposed. The method outlined in Table XLV is comparatively simple and gives good results. Confirmatory tests are suggested by Tables XLIII and XLIV. A few additional characteristic tests are suggested below.

Ruthenium is best recognized by the delicate blue color produced when the solution of the trichloride is treated with H_2S. This color is possibly caused by the formation of the dichloride.

Alkali chlorides precipitate K_2RuCl_6, violet, from concentrated solutions. This double chloride is difficultly soluble in water, but is hydrolyzed in boiling water, giving black insoluble oxychloride.

Ruthenium trichloride reduced with a small amount of zinc gives an azure blue color probably due to $RuCl_2$; an excess of zinc produces metallic ruthenium as a fine black powder.

If a ruthenium solution is made alkaline with ammonia, a little sodium thiosulfate added and the mixture boiled for two or three minutes, a color develops varying from rose to red-purple. This test may be applied in the presence of iridium.

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[1] Wöhler and Witzmann, *Zeit. anorg. Chem.* **57** 323 (1908).

[2] Wöhler and Streicher, *Ber.* **46** 1577 (1913).

TABLE XLV

Qualitative Separation of the Platinum Group Metals

The solution of the chlorides is acidulated, heated, and then coldly saturated with H_2S. Filter, wash, warm with $(NH_4)_2S_x$ and filter.						
Residue, may contain sulfides of Ru, Rh, Pd, and Os. Fuse with KOH + $KClO_3$, extract with water, and filter.				Solution may contain [illegible] salts of Au, [illegible], Sn, Pt, Ir, As. Acidify with HCl [illegible] [illegible] [illegible] and [illegible]. Extract [illegible] water [illegible] arsenate. Reduce [illegible] with Zn and HCl [illegible] [illegible] with HNO_3 and HCl [illegible]. Heat [illegible] to dryness, and treat with dilute aqua regia.		
Residue. Ignite in hydrogen and extract with HNO_3. Insoluble portion may contain Rh or Pd. Add aqua regia.		Solution, may contain Ru and Os. Neutralize with HNO_3 and filter.				
Residue: Rh.	Solution is evaporated, dissolve the residue in water, nearly neutralize with NaCl treated add $Hg(CN)_2$ solution, a white precipitate is $Pd(CN)_2$	Precipitate, black, is an oxide of Ru	Filtrate distilled with HNO_3; volatile OsO_4 passes over	Residue: Iridium	Solution. Evaporate to dryness on a steam bath with excess of NH_4Cl. Treat with alcohol, filter.	
					Residue: Platinum	Filtrate: gold is precipitated by adding $FeSO_4$ solution

To a ruthenium solution add an alkali carbonate to alkaline reaction, then a little KNO_2 solution and heat for a moment; cool completely, add a drop or two of colorless ammonium sulfide, and shake the tube. A red color develops. This test is sensitive and may be used in the presence of all other platinum metals.

Rhodium forms the hydrated chlororhodite $Na_3RhCl_6 \cdot 12H_2O$, when heated with NaCl and chlorine. It dissolves in water, forming a rose-red solution. Although this color is quite characteristic, under some conditions it is easily confused with the color produced by ruthenium.

Rhodium trichloride treated with KNO_2 yields a precipitate which is pale yellow, with a faintly greenish cast. This precipitate is characteristic, but it does not give a sensitive test for rhodium because the double nitrite is somewhat soluble. This salt dissolves rather slowly in concentrated HCl, giving a raspberry-red solution, the color being characteristic but not intense.

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[1] J. N. Friend, *Textbook of Inorganic Chemistry*, Vol. IX, p. 342. The method given by Mylius and Mazzucchelli, *Z. anorg. Chem.*, **89**, 22 and 77 (1914), affects a satisfactory separation without the use of ammonium polysulfide, but it does not include ruthenium and osmium.

TABLE XLVI — *Reactions of Platinum Group Metals in Compact Form.*[1]

	RUTHENIUM	RHODIUM	PALLADIUM	OSMIUM	IRIDIUM	PLATINUM
Boiling with aqua regia	Dissolves slowly	Insoluble except in some alloys	Soluble	Soluble yielding OsO_4	Insoluble	Soluble
Boiling with nitric acid	Insoluble	Insoluble	Slowly soluble	Insoluble	Insoluble	Insoluble
Boiling with sulfuric acid	Insoluble	Insoluble	Slowly soluble, forms $PdSO_4$	Insoluble	Insoluble	Attacked slightly
Fusion with $KHSO_4$	No action [2]	Forms soluble $K_6Rh_2(SO_4)_6$	Dissolved	Partly oxidized to OsO_4	Oxidized but not dissolved	Slightly attacked
Fusion with $KOH+KNO_3$	Forms K_2RuO_4, green, soluble in water giving orange solution	Oxidized	Oxidized	Dissolved forming K_2OsO_4	Oxidized to soluble and insoluble iridates	Attacked
Treatment with iodine solution	—	—	Black stain	—	—	No action

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[1] J. N. Friend, *Textbook of Inorganic Chemistry*, Vol. IV, p. 331.

[2] There is some indication that ruthenium is oxidized to RuO_2.

Palladium is the only one of the rare platinum metals which reacts with $Hg(CN)_2$. The precipitate, $Pd(CN)_2$, is white with a yellowish tint, gelatinous and readily soluble in both KCN and NH_4OH.

The solution of an iodide added to a palladous solution precipitates black PdI_2, rather slowly soluble in an excess of alkali iodide. Rhodium may also precipitate if present in fairly large quantities.

Dimethylglyoxime gives a pale yellow flocculent precipitate, with palladium salts. None of the other platinum metals will precipitate in the cold; copper does not interfere but gold and nickel must be absent.

Osmium in the metallic state sublimes at white heat without melting, and on heating in air or in oxygen it produces OsO_4, volatile, and extremely poisonous. This oxide is soluble in water and from this solution, $FeSO_4$ precipitates $Os(OH)_4$, black; sulfurous acid produces colors ranging from yellow to green to blue, the latter being the color of $OsSO_3$; metallic zinc precipitates osmium as a black powder, which is the only one of the platinum metals that dissolves in hydrogen peroxide.

Any osmium compound heated with concentrated nitric acid yields vapors of OsO_4. If OsO_4 is distilled into water, the solution slightly acidified, and ether or amyl alcohol added, a blue color results. This test is said to detect one part OsO_4 in a million parts of water.

A solution of a chlorosmate or of the tetroxide acidified with HCl and warmed with an excess of thiocarbamide, yields a deep rose color. This test is said to detect 1 part osmium to 100,000.[1]

Iridium tetrachloride, treated with excess of alkali hydroxides, gives a green solution with a small black precipitate of the double chloride. On heating the solution first becomes red, then deep azure blue, due to the precipitation of $Ir(OH)_4$. This test distinguishes iridium from platinum.

Alkali chloriridates are reduced by $FeSO_4$, or $SnCl_2$, the solutions being decolorized and chloriridites formed. These salts crystallize out on cooling.

Platinum salts are reduced by $FeSO_4$, or $SnCl_2$, the metal finally resulting.

Platinic solutions yield with $SnCl_2$ a blood-red color if the solution is concentrated, or a golden brown in a dilute solution. The color is extracted with ether. This test distinguishes platinum from palladium, iridium, gold, or iron, but it must be carried out in the absence of filter paper or other organic matter.

Platinic chloride is not reduced by oxalic acid, another method of distinguishing platinum from gold.

Potassium iodide gives a test for platinum which is very delicate. When added to a solution of platinum chloride a color appears which varies from rose red to brown; or black PtI_4 may be precipitated. An excess of KI produces K_2PtI_6, brown, sparingly soluble. Iron, copper, and oxidizing agents interfere with this test.

Estimation. — The quantitative determination of the metals of the platinum group is a task which requires long and skillful effort on the part of the analyst. Many schemes of separation have been proposed and used,

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[1] Tschugaev, *Compt. rend.* **167** 235 (1918).

TABLE XLVII

Reactions of Chlorides of the Platinum Group Metals[1]

	$RuCl_3$	$RhCl_3$	$PdCl_2$	$OsCl_4$	$IrCl_4$	$PtCl_4$
Color[2]	Dark brown	Red	Brownish-yellow	Yellow	Dark brown	Yellow
H_2S[1] at 80°C	Azure blue color, slow forming	Rh_2S_3, brownish-black	PdS, brownish-black	OsS, brownish-black	Ir_2S_3, brownish-black	PtS_2, brownish-black
Ammonium sulfide	Ru, dark brown, difficultly sol. in excess	Rh_2S_3, dark brown, insol. in excess	PdS, black, insol. in excess	Dark ppt. insol. in excess	Ir_2S_3, brown, sol. in excess	PtS_2, brown, sol. in excess giving $(NH_4)_2PtS_3$
Caustic alkalies	Black ppt. insol. in excess	$Rh(OH)_3$, yellow-brown, sol. in excess	Basic salts, yellow-brown, sol. in excess	$OsO_2 \cdot 2\,H_2O$, brownish-red	Double chloride, brownish-black ppt. sol. green	Dark ppt. of $PtO_2 \cdot (H_2O)$
NH_4OH[2] on warming	Green color	Slowly decolorized	Decolorized	Yellowish-brown ppt.	Bright color	Slowly decolorized
Saturated[2] NH_4Cl	Brown ppt.	No ppt.	No ppt.	Red ppt.	Black ppt.	Yellow ppt. $(NH_4)_2PtCl_6$
Saturated KCl	Violet ppt. cryst. K_2RuCl_5	Red ppt. cryst. K_3RhCl_5	Red ppt. K_2PdCl_4	Brown ppt. cryst. K_2OsCl_6	Brownish-red ppt. K_2IrCl_6	—
KI solution[2] 1 : 1000	No change	No change	Dark ppt. PdI_2, sol. in excess	No change	Yellow color	Red-brown color; slow forming
$Hg(CN)_2$ sol.	No change	No change	White ppt. $Pd(CN)_2$	No change	No change	No change
KCNS, 1 per cent	Dark violet color	Yellow color	Unchanged	Unchanged	Decolorized	Increased yellow
Hydrazine[2] in HCl	Yellow color	Yellow color	Pd. Black ppt.	No change	Yellow color	Pt. Black ppt.
Dimethyl-glyoxime[2]	Yellow ppt.	No change	No change	No change	No change	No change
Metallic zinc	Ru ppt.	Rh ppt.	Pd ppt.	Os ppt.	Ir ppt.	Pt ppt.

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[1] J. N. Friend, *Textbook of Inorganic Chemistry*, Vol. IX, p. 332.

[2] Metallic chlorides in dilute solution. See Mylius and Mazzucchelli, *Zeit. anorg. Chem.* **89** (1914).

Table XLVIII

Quantitative Separation of Metals of the Platinum Group

<table>
<tr><td colspan="7">Treat with aqua regia. If an insoluble residue remains, fuse in a nickel crucible with Na_2O_2 and dissolve the melt in HCl. Mix the two solutions, make alkaline, and distill in chlorine.</td></tr>
<tr><td rowspan="5">Volatile portion is collected in NaOH solution. Ru and Os. Acidify and add H_2S. Dry the sulfides and ignite in a stream of oxygen. RuO_2 remains behind and OsO_4 is collected in NaOH and alcohol.</td><td colspan="6">Remaining solution is boiled to expel chlorine. Add concentrated solution of NH_4Cl and two-thirds its volume of alcohol.</td></tr>
<tr><td colspan="3">Precipitate: Pt, Ir, some Rh, and traces of Pd. Ignite in hydrogen and extract with aqua regia diluted with four parts water.</td><td colspan="3">Filtrate: Rh, Pd, Cu, Fe, Ni, a little Pt, and Ir. Nearly neutralize with NH_4OH; add H_2S.</td></tr>
<tr><td colspan="2">Residue: Rh, Ir. Fuse with $KHSO_4$, extract with water, and dilute H_2SO_4.</td><td rowspan="2">Solution contains platinum with possibly traces of Pd, Rh and Ir.</td><td colspan="2">Precipitate: sulfides of Au, Cu, Pd, Rh. Ignite and digest with HCl. Repeat.</td><td rowspan="2">Filtrate: Fe, Ni, some Au, and Rh. Evaporate to dryness with HNO_3 and ignite. Extract Fe and Ni with HCl. Ignite residue (B) and combine (A) and (C).</td></tr>
<tr><td>Residue: Ir with possibly a trace of Rh.</td><td>Solution: Rh (A) boil with Na_2CO_3. Acidify with HCl. Ignite and combine with Rh from (B) and (C).</td><td>Residue: Rh (C) combine with (A) and (B).</td><td>Filtrate: Cu and Pd. Add KCl and alcohol when Pd is precipitated as K_2PdCl_4.</td></tr>
<tr><td colspan="6">Combined residues (A) (B) (C) contain Rh and Au. Digest in aqua regia, when gold dissolves and rhodium is left as a residue.</td></tr>
</table>

the one suggested by Mellor[1] is relatively simple and satisfactory. It is shown in Table XLVIII. After the separations are made the quantitative determinations may be made as follows:—

Ruthenium may be weighed as the metal, after precipitation with magnesium and washing with dilute H_2SO_4. It is best to ignite in hydrogen and cool in CO_2. Some of the base metals will also be precipitated by magnesium, so it is probably better to precipitate ruthenium with hydrogen sulfide. This may be accomplished by thoroughly saturating the solution with H_2S, then setting aside until the blue color disappears. It is necessary to reduce in hydrogen, and if the amount of ruthenium is large the hydrogen should be displaced by carbon dioxide or nitrogen free from oxygen.

Rhodium may also be determined as the metal, the treatment being similar to that described for ruthenium. It is probably best precipitated with H_2S from hot solution. It is generally unnecessary to allow the solution to stand in order to produce complete precipitation.

The metal may be produced by reducing a solution with hydrazine hydrate in hot alkaline solution. The precipitate is dried, ignited in air, then in hydrogen, and cooled in CO_2.

Palladium may be precipitated with hydrogen sulfide, mercuric cyanide, or dimethylglyoxime. Either of the last two reagents separates palladium from most of the other elements, but lead and copper are troublesome. The precipitate may be cautiously ignited to the metal, then reduced in hydrogen and the hydrogen replaced by carbon dioxide or nitrogen. Reduced palladium may be cooled in the air, if a few drops of formic acid are added to reduce any oxide. The metal is then dried in an oven and weighed.

Metallic palladium is precipitated from hot dilute solutions by a hydrazine salt in acid solution; also by passing acetylene through an acidified solution.

Osmium is satisfactorily determined by acidifying an alkali osmate solution in the presence of alcohol. After 10–12 hours the precipitate is removed and reduced in hydrogen.

A solution of the tetroxide may be reduced with formaldehyde, the precipitate being heated in hydrogen.

Distill OsO_4 into ammonium hydroxide, add hydrogen sulfide, and evaporate the entire solution to dryness, then ignite the residue in hydrogen and weigh the metal.

Volumetrically a solution of the tetroxide is acidified with sulfuric acid, potassium iodide added and the liberated iodine titrated with thiosulfate.

Iridium is quantitatively removed from its solutions with great difficulty. A method is given for evaporating with aqua regia, adding ammonium chloride, then drying and igniting the precipitated $(NH_4)_2IrCl_6$, but it fails to remove all iridium. Probably a better method consists in thorough treatment with H_2S in a pressure bottle, then igniting the sulfide, and reducing with hydrogen.

Iridium may be determined in the presence of platinum as follows:

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[1] Mellor, *A Treatise on Quantitative Inorganic Analysis.*

the alloy is heated with ten times its weight of lead and the button digested with hot nitric acid until the lead is removed; the residue is digested with aqua regia which has been diluted with five parts of water, then the iridium metal is washed, ignited, and weighed.

Platinum may be determined as the metal by igniting the sulfide, obtained by the action of H_2S on an acidified solution of the chloride.

Ammonium chlorplatinate may be precipitated by evaporating a neutral solution of $PtCl_4$ just to the point of crystallization, then adding an excess of a saturated solution of NH_4Cl. Add alcohol, let stand twenty-four hours; filter, wash with 80 per cent alcohol, dry, and weigh. The precipitation of platinum by this method is not quite complete. The precipitate may finally be ignited in a stream of hydrogen, but the ignition should never be made in air because of loss of platinum, probably through the volatility of $PtCl_2$.

Volumetrically, platinum may be determined by adding KI to a solution of platinic chloride or alkali chlorplatinate. The iodine liberated is titrated with thiosulfate, one molecule of platinic chloride liberating a molecule of iodine. This method is not extensively used.

The plan for the quantitative separation of the metals of the platinum group,[1] given in Table XLVIII, must be considered as an approximation. It may be necessary to repeat the fusion with Na_2O_2 in dissolving the melt in HCl. Heating the solution must be avoided to prevent loss of OsO_4. It is probable that the chlorine distillation will have to be repeated several times in order to remove all of the ruthenium. Precipitation of platinum and iridium by means of ammonium chloride is never complete and the precipitate is always contaminated with rhodium and palladium.

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[1] For a scheme which is better suited to the analysis of alloys see the method of Deville and Stas as modified by Mylius and Foerster, *Ber.* **25**, 665 (1892).

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