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This volume correlates basic data on rarer metals for the busy professional man and student. It is suitable as a reference text or for supplementary reading in science and engineering courses. Special consideration has been given to rarer elements upon which much of our future progress may depend.

Some twenty elements, excluding the metals of the rare earths on which there is extensive literature, are discussed briefly, including some of the interesting and important practical applications of these elements.

Good illustrations, an up-to-date bibliography and a detailed index and greatly to the value of this text on the less familiar elements.

RARER METALS

By

JACK DE MENT
Research Chemist,
Fluorescence Laboratories

and

H. C. DAKE
Editor,
The Mineralogist

With Foreword by

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Columbia University

1946

CHEMICAL PUBLISHING COMPANY, INC.

BROOKLYN NEW YORK

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1946

CHEMICAL PUBLISHING CO., INC.

BROOKLYN NEW YORK

FOREWORD

Metallurgy had its beginnings before the days of the ancient Egyptians. For many hundred years, there were but six recognized metals: gold, silver, copper, iron, lead, tin and mercury. The outstanding characteristic of the metallurgy of the twentieth century is the commercialization of a large number of rarer metals. Rhodium makes the best mirrors; columbium corrects intergranular corrosion of stainless steel; tellurium improves the qualities of lead and of rubber; tungsten makes our toughest steels; beryllium renders copper hard and fatigue-resistant; barium is our best electron emitter; uranium the most fascinating of all rare metals. Many more examples might be cited. The rare-metal art has advanced to a stage where it is securely established. May the account of the twenty metals in the pages to follow stimulate the young metallurgist and scientist to further discoveries and useful applications.

COLIN G. FINK

Preface

For some years, there has been a need for a concise book in which the mineralogy, chemistry, physics, and technology of the less familiar elements are briefly described.

It is the intention in this volume to compile basic data on rarer metals for the busy professional or student. It is suitable as a text or for supplementary reading in science and engineering courses. Special consideration has been given to rarer elements upon which much of our future progress may depend.

As may be expected, in a work of this nature, no attempt has been made to treat the subject exhaustively, nor have all aspects of all "rare" elements been discussed. The present work discusses some 20 of the less-familiar elements, excluding the metals of the rare earths. The authors have stressed many of the interesting and important practical applications of each of these elements.

A comprehensive survey of analytical methods is beyond the scope of this book. Procedures now employed can easily be found in any standard reference work on analytical chemistry. However, newer tests, such as those of microchemistry and fluorochemistry have been discussed. Some stress has been laid upon specific tests which can be performed rapidly with simple equipment and good results.

The authors gratefully acknowledge the help of Professor Colin G. Fink of Columbia University, who is a pioneer in the field of rarer elements.

Many commercial firms have supplied us with information and photographs. Due credit is given them in the text and illustrations. The list of literature references for less important metals has been kindly furnished by Mr. R. B. Gordon of the

John Crerar Library in Chicago. The Mineralogist Magazine and the Fluorescence Laboratories, both of Portland, Oregon, have been kind in supplying photographs and unpublished information.

The authors will appreciate having their readers point out any errors of omission or commission present in this volume.

JACK DE MENT
DR. H. C. DAKE

Portland, Oregon

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CHAPTER I

BERYLLIUM

History

During the chemical analysis of the mineral beryl, in 1797, Vauquelin found an unknown earth metal whose chemical properties closely resembled those of aluminum.[1] The new substance was characterized by the sweet taste of its salts. It was obtained after removing the silica by precipitating with potassium carbonate and then treating with potassium hydroxide solution. It differed from aluminum in that it did not form alums, nor was it precipitated by ammonium oxalate or ammonium tartrate. The new element was separated from aluminum by boiling with potassium hydroxide, when the aluminum was dissolved. The residue was found to be soluble in ammonium carbonate.

Vauquelin called the element *la terre du beryl,* after the mineral from which it was first obtained. However, the editors of the journal *Annales de chimie et de physique,* in which the first report was published (1798), suggested the name *glucine* for the element because of the sweet taste of its soluble salts. Vauquelin used this name with reluctance. Later it was called *beryllium* and, although *glucinium* is still used in certain countries, *beryllium* is the preferred name.[2]

Mineralogy

Beryllium is not found native. It does not occur in large deposits but is widely scattered in various rocks and minerals. Beryllium minerals are frequently associated with pegmatite granites. Some beryllium minerals such as beryl and emerald were known 5000 years before the element itself was discov-

ered. Beryllium is also a constituent of a number of semi-precious gems. Some of the principal minerals are listed in table 1.

Beryl

Beryl is the most important commercial beryllium mineral. It contains 14 per cent beryllium oxide, 19 per cent aluminum oxide, and 67 per cent silicon dioxide. Beryl is a common mineral of pegmatite veins. It is also found in clay slate and mica schist. Beryl goes over into mica and kaolin. Beryllium appears as a constituent of secondary minerals, such as bertrandite, herderite, or beryllonite. Beryl forms pale blue crystals or crystalline masses. Emerald, aquamarine, and morganite are gem varieties of beryl.

Beryllium is sometimes found in small amounts together with monazite and other rare earth sands, and in aluminous schists. Sulfurous spring waters, throughout the world, contain varying quantities of beryllium.

TABLE 1

BERYLLIUM MINERALS

Name	*Per Cent BeO**
Bertrandite	40–43
Beryl	11–15
Beryllonite	19–20
Chrysoberyl	19–20
Euclase	17–18
Hambergite	53–54
Helvite	13–14
Herderite	15–16
Leucophanite	10–12
Meliphanite	10–14
Phenacite	44–46
Trimerite	16–17

* BeO contains 36.05 per cent Be.

Beryl is a common constituent of the pegmatites of New England, where it is often found in the form of enormous single crystals. At Albany, Maine, a single crystal was found weighing over 18 tons. Although the large crystals often yield a considerable amount of beryllium, they cannot be relied upon as a commercial source.

There is a moderately large amount of low-grade beryllium ore in New England which can be treated to satisfy the commercial demand. In recent years, much of the beryllium used in the United States originated from beryl mined in the Black Hills of South Dakota. A considerable amount of beryl is also obtained as a by-product from the feldspar mines in various eastern states.

Lately, there has been a steady increase in the demand for beryllium. In 1934, the monthly consumption of beryl was approximately 35 tons per month and its price at the mine ranged from $25 to $35 per ton. Since then, the demand has increased substantially. The use of steel-like beryllium-copper alloys is rapidly gaining favor for the manufacture of small machine parts.

It is generally recognized that a limiting factor in the growth of the beryllium industry is the scarcity of the ore. For the present, at least, beryl constitutes the sole commercial source of beryllium. Low-grade deposits of beryllium occur in various parts of the United States, and, very likely when beryl alone can no longer fill the need, a means will be found to utilize the lower-grade deposits by improved milling methods and advanced metallurgical processing. During 1941, about 1600 tons of beryl ore were imported from Brazil and Argentina at $35 per ton.

The scarcity of beryllium ores is not the only reason for its limited use. In addition, beryl is highly refractory and beryllium itself is extremely reactive at elevated temperatures. Finally, the refining of the metal is a lengthy process.

For a long time, difficulties in chemical analysis rendered uncertain the evaluation of low-grade beryllium ores. But now

this uncertainty has been removed by the introduction of improved methods of assay. World-wide search for beryllium ores during the past decade has assured the beryllium industry of a dependable, though moderate supply. It does not appear at present that beryllium will become a low-priced metal in the near future. Small as it is, the beryllium industry of the United States is the largest in the world. Much of the recent research carried on in this field has been done in the United States and Germany.

Physical Properties

The physical properties of beryllium have long been described in the literature, although in many cases erroneous statements were made. Beryllium is a grayish, hard, brittle metal, darker in color than aluminum. It melts at about 1285°C and boils at about 1500°C. Because of its high melting point and low atomic weight (9.05) its heat of fusion is higher than that of any other known metal.

Some authors have stated that small quantities of beryllium of 99.99 per cent purity may be drawn into wire and cold-rolled into sheet. Modern beryllium technologists doubt that even a pound of the metal has been cold-rolled into sheet or drawn into wire. However, at higher temperatures, beryllium is comparatively ductile and may be rolled into sheet. An addition of 0.3 per cent of titanium or zirconium acts as a scavenger, removing the embrittling traces of BeO.[3]

Beryllium has a low specific gravity, about 1.85. It crystallizes in the hexagonal system as small lamellae or prismatic tablets. Its coefficient of linear expansion, $12.3 \times 10^{-6(\text{at } 20°C)}$, is approximately one-half of that of aluminum. It has a hardness of 60 to 140 Brinell.

Beryllium is characterized by two lines in the visible spectrum, one at 4572.0Å in the blue and another at 4488.5Å in the indigo. Young's modulus for beryllium is about 40,000,000 lb per square inch. His modulus of elasticity is about 42,000,000

lb per square inch, its shearing stress 38,600 lb per square inch and its electrical conductivity 43.1 per cent that of copper. The single ionization potential of beryllium is 9.28 volts.

Beryllium has an atomic number of 4 and an atomic weight of 9.02. It occurs as a mixture of two isotopes, one of atomic weight 8 making up 0.05 per cent of its mass, and the other of atomic weight 9. It is seventeen times as transparent to X-rays as aluminum and emits neutrons when heavily bombarded with alpha particles.

Chemical Properties

Pure beryllium is stable in dry air and pure oxygen at room temperatures. When finely divided and blown into a flame it burns with brilliant scintillations. When beryllium is heated in air it oxidizes slightly and forms a protective covering resembling that formed on aluminum under the same conditions. Beryllium is not attacked by hot or cold water for this reason.

Beryllium is bivalent. It combines with the halogens. It is soluble in mineral acids.

Compounds

The physical and chemical properties of beryllium compounds are similar to those of aluminum compounds, e.g., beryllium oxide, like aluminum oxide, is white and insoluble in water.

When beryllium is heated with molten selenium, tellurium, or sulfur, it forms a selenide, telluride or sulfide. Beryllium also combines with fused phosphorus and arsenic, forming phosphides and arsenides. With nitrogen, beryllium forms a nitride, Be_3N_2; and with carbon a carbide, Be_2C.

When beryllium salts are allowed to react with ammonium carbonate, a white precipitate of basic beryllium carbonate forms. This precipitate is freely soluble in excess ammonium carbonate and reprecipitated on boiling. This reaction may be used to distinguish beryllium from aluminum.

Ammonium hydroxide and ammonium sulfide, as well as

fixed alkali hydroxides and alkaline earth hydroxides, precipitate flocculent beryllium hydroxide. It is soluble, much like aluminum hydroxide, in an excess of alkali, but not in ammonium hydroxide. Boiling reprecipitates the dissolved hydroxide almost completely.

Beryllium salts are precipitated from their solutions by barium carbonate in the cold. When solutions of beryllium sulfate and potassium sulfate are mixed and allowed to crystallize slowly, a nearly insoluble sulfate forms, which has alum-like properties. The halides are readily hydrolyzed by water, the hydrolysis of chlorides, bromides, and iodides being practically complete.

Extraction from Beryl

a. *French Method.* Finely ground beryl is mixed with sodium fluosilicate and heated to 850°C. The double fluoride, Na_2BeF_4, is formed. The aluminum in the mineral is converted to cryolite, Na_3AlF_6. The silica remains unaffected. The reacted mass is treated with boiling water to dissolve the beryllium salt. If desired, impurities such as iron are removed by converting the fluorides to sulfates and fractionating.[4]

b. *German Method.* As in the French method, the finely ground beryl is sintered with sodium fluosilicate for several hours at 850°C.[5] The Na_2BeF_4 is extracted with water; any iron that may go into solution is precipitated by bubbling air through the solution. Next, caustic lime is added to precipitate beryllium hydroxide, $Be(OH)_2$, together with some calcium fluoride. The precipitate is treated with hydrofluoric acid. Calcium fluoride remains undissolved and is filtered off. The filtrate is evaporated and the residue, beryllium oxyfluoride, $5BeF_2.2BeO$, is fed directly into a fused electrolytic bath of beryllium oxyfluoride plus barium fluoride (equal parts). Beryllium is deposited on the iron cathode. The barium fluoride is added to facilitate the separation of beryllium from the melt.

c. *American Method.* Finely ground beryl is chlorinated at

500°C for several hours: Iron, aluminum and other impurities form volatile chlorides which are eliminated. The temperature is then raised to about 900°C, and the beryllium chloride, $BeCl_2$ passes into the condenser. The residue is largely silica. The beryllium chloride thus produced is electrolyzed in a fused mixture of $BeCl_2$ and NaCl.[6]

Technology

Beryllium possesses an unusual combination of properties. It is an ideal light metal, being about one-third lighter than aluminum, and yet more rigid than steel. The remarkable resistance to corrosion makes beryllium suitable for numerous applications. Its thermal coefficient of expansion is about the same as that of cast iron, therefore it might serve well for piston heads in internal combustion engines. Beryllium alloys with aluminum, copper, iron, nickel, cobalt, silicon and a few other metals. The alloy of copper and beryllium is a well-established commercial product, with a growing list of applications. The limitations in the uses of beryllium and its alloys appear to be fairly well known.

For some years there has been confusion regarding the true properties and possibilities of beryllium and its alloys. Stott [7] has pointed out that numerous exaggerated statements have been made regarding the properties of this metal during the past twenty years.

In the early stages of beryllium production in the United States, in 1925, research was directed toward the development of a light-weight structural metal. The studies indicated that the metal was not sufficiently ductile to be used for structural purposes. However, it is highly probable that light alloys of beryllium will be developed in the near future for use in airplane construction, where weight and strength are important factors.

A great deal of work has been done on non-ferrous beryllium alloys. Alloys of very high tensile strength have been prepared in the laboratory. Beryllium alloyed with iron is becoming

increasingly important. Recently, industry has made wider use of beryllium-iron alloys for munitions and vital airplane engine parts. An alloy of 20 per cent beryllium and 80 per cent iron, known as *ferroberyllium*, has found some use in "cementing" steel. Beryllium readily dissolves in iron, and with suitable technique a maximum penetration of 20 to 25 mm can be secured—the case-hardened surface having a hardness of over 1000 Brinell.[8]

An alloy in actual use is nickel containing 2.5 per cent beryllium, which hardens to 600 Brinell after quenching from 1100°C and drawing at 400° to 500°; another is 18 carat gold, hardened to 300 Brinell by the addition of beryllium. Steel containing 36 per cent nickel and 1 per cent beryllium is rustless and machinable, and, like Invar, it does not expand or contract when heated within the room temperature range. Beryllium forms a eutectic compound with iron at a concentration of 9.2 per cent beryllium, melting at 1150°C. This alloy can be refined in grain by heat treatment.

Tin-beryllium alloys, containing 0.2 per cent beryllium, are 20 per cent less ductile than pure tin, are slightly harder and have improved bending strength. When the amount of beryllium in tin is increased, primary crystals of beryllium are formed in a grounding mass, which contains only a few tenths of 1 per cent of beryllium. Additions of beryllium to aluminum-magnesium alloys prevent loss of magnesium by oxidation during melting, prevent surface defects on castings and inhibit discoloration during heat treatment. The beryllium promotes coarser structure, affects mechanical properties and increases the time of heat treatment. These disadvantages are eliminated by adding small amounts of titanium. Only 0.02 per cent beryllium is required in these alloys.

To produce a hard strong alloy of beryllium and magnesium for aircraft and other purposes has been the aim of numerous investigators. But all attempts have so far been futile. The main difficulty lies in the fact that the melting point of beryl-

lium (1282°C) is almost 200° above the boiling point of magnesium (1107°C). Another factor is that molten magnesium will not dissolve solid beryllium. This has been attributed to the presence of a tenacious, refractory oxide film (BeO) protecting the beryllium particles added to the molten magnesium. To test this theory operations were carried out in the absence of air and in the presence of that very inert gas, argon. No alloy was formed. Other attempts include codeposition of the two metals from a fused salt bath, pressed sintered rods made by powder metallurgy, and reduction of beryllium fluoride and other beryllium compounds with magnesium metal. The problem is still unsolved.

Beryllium-Copper Alloy

One of the most interesting and important beryllium alloys is the beryllium-copper alloy. Beryllium increases the hardness of copper more effectively than any other known agent.[9] An addition of only 2.25 per cent beryllium results in an alloy six times as strong as pure copper. This remarkable strength is gained with less sacrifice of electrical conductivity than is the case when hardening agents, such as tin or silicon, are employed. Beryllium-copper alloy can be stressed 50 per cent more than copper without taking a set.

Beryllium-copper is finding use in many articles, e.g., control apparatus, aviation instruments, and communication devices. The alloy can also be used for making frictional and wearing parts, such as bushings, cams, and sleeving. One aviation engine manufacturer reported the successful application of beryllium-copper alloy in tappet roller bushings at a bearing pressure of 9000 lb per square inch.

Under laboratory conditions beryllium-copper has a corrosion resistance approximately equal to that of deoxidized copper. After undergoing a salt spray test for 6 months and a four-day alternate immersion test in warm 10 per cent sulfuric acid solution, beryllium-copper suffers a slightly greater loss

in weight than does deoxidized copper, but if hydrochloric acid is used for the alternate immersion test, the deoxidized copper loses a little more weight than copper-beryllium.

Tests were conducted for 10 months on the behavior of beryllium-copper specimens exposed at half tide elevation in Long Island Sound, under circumstances which are most destructive for metals. Some specimens were cold-rolled and heat-treated, others were quenched from 800°C and heat-treated without intermediate rolling.

The results indicated that the corrosion resistance of beryllium-copper is not affected by heat-treatment. The tests also revealed that beryllium-copper is somewhat more resistant to the action of sea water than is deoxidized copper. No intergranular corrosion was observed. The ductility of the alloy was unaffected by the ten months' exposure to sea water.

In the presence of halogens, especially at higher temperatures, beryllium escapes from the surface of the alloy, apparently because of the high volatility of its halides. This property prevents the use of beryllium-copper where exhaust gases from bromine-treated lead tetraethyl gasoline are present.[10]

Beryllium-copper ball bearings are used in places where magnetic effects must be reduced to a minimum. There are now on the market beryllium-copper watches that are unaffected by a magnetic field. The alloy is also used for making fuse springs in shells and solderless terminals for the automobile industry. It accelerates the assembly of distributors and other electrical equipment because of its non-magnetic nature.

A specialized application of beryllium-copper is in the manufacture of low-sparking "safety" tools. A spark from a steel tool might cause a serious explosion, e.g., while repairing a gasoline tank, therefore, non-ferrous tools are essential. Various non-ferrous alloys have been used for making hammers and cold chisels, but most of these alloys lack the hardness and toughness of beryllium-copper. Several leading chemical and oil concerns now use beryllium copper tools. The variety

of safety tools for use in the presence of dangerous gases or liquids ranges from wire brushes to wrecking bars, and includes axes, pitchforks, pliers, wrenches, hammers, chisels, etc. No metal tool completely eliminates the spark hazard, but the beryllium-copper alloy greatly reduces it.

Beryllium-copper alloys are improved by adding 0.5 per cent cobalt, and by keeping the beryllium content down to 2.0 per cent. Such an alloy has excellent electrical conductivity and age-hardening qualities. Its hardness is approximately the same as that obtained by heat-treatment of the simple beryllium-copper alloy. It is an interesting fact that the beryllium content of the cobalt alloy can be reduced to as little as 1.8 per cent without an appreciable change in hardness.

Another beryllium-cobalt alloy has been prepared, in which the cobalt content is greater than the beryllium content, both elements being alloyed with copper. The best known example of this type is an alloy containing about 1.5 per cent beryllium, 2.6 per cent cobalt, and the remainder copper. This alloy is noteworthy because of its high electrical conductivity and heat resistance.[11]

The latter alloy has had satisfactory use as a substitute for phosphor-bronze in electrical contact springs for electric range switches, which must be able to withstand considerable overheating. In one test, contact springs of the beryllium alloy were vibrated 500,000 times, at a fiber stress of 70,000 lb per sq. in., without failure. This test indicates excellent fatigue properties.

The very high fatigue resistance of beryllium-copper alloys is due partly to a high tensile strength and elastic limit and partly to some other property of the alloys, acquired during precipitation hardening. It has been suggested that the very low "elastic drift," or hysteresis, results from the relief of stresses when the metal is heated to about the same temperature as that required for precipitation hardening.

The beryllium-copper alloys are also said to exhibit remark-

able wear resistance when subjected to heavy-pressure rubbing loads.

At the present time, the rapidly increasing demand for beryllium comes from its use in the manufacture of many small machine parts. By far the largest outlet is for copper-beryllium springs and small parts in business machines, such as typewriters and calculating machines. Next in importance is its use in the construction of control instruments. Recent aircraft instrument developments promise to make this an even more important field for the application of beryllium.

Certain properties of beryllium alloys make them valuable for use in Bourdon springs for pressure gages, especially for oxygen pressure gages, which must resist corrosion and retain resistance to fatigue. Other metals, especially heat-treated alloys, cannot be employed because they tend to creep or lengthen after long or repeated stress.

Many uses for beryllium alloys have been described by Tyler.[12]

At present, in America as well as in Europe, much of the beryllium-copper alloy is made directly by electric smelting rather than by first producing the beryllium metal electrolytically and then adding it to a molten copper bath. The present procedure is similar to the old process of the Cowles brothers,[13] who produced the golden alloy of copper and aluminum some time before Hall and Heroult invented their aluminum metal process.

The Brush Beryllium Company produces copper-beryllium alloy in an electric furnace.[14] Beryllium oxide, BeO, is reduced with carbon at above 1600°C. As the beryllium metal is formed, it is taken up by molten copper below the reaction charge. The Beryllium Corporation of Pennsylvania proceeds as follows: An electric arc furnace is charged with a mixture of finely divided beryllium oxide, carbon and copper; the mass provides sufficient reaction material near the arc to produce a drop in temperature down to at least 1285°C. Sufficient reaction material remains above the arc to trap any beryllium metal

vapor rising from the region of the arc. The temperature below the level of the arc is regulated so as to avoid excessive material losses. At intervals pieces of copper metal are fed onto the top of the reaction mass above the arc. These pieces melt and the liquid copper in its downward path washes out any beryllium metal caught in the mass.[15] The molten mixture of copper and beryllium metals is tapped off at the bottom of the electric arc furnace. The Be is obtained in the form of a copper alloy.

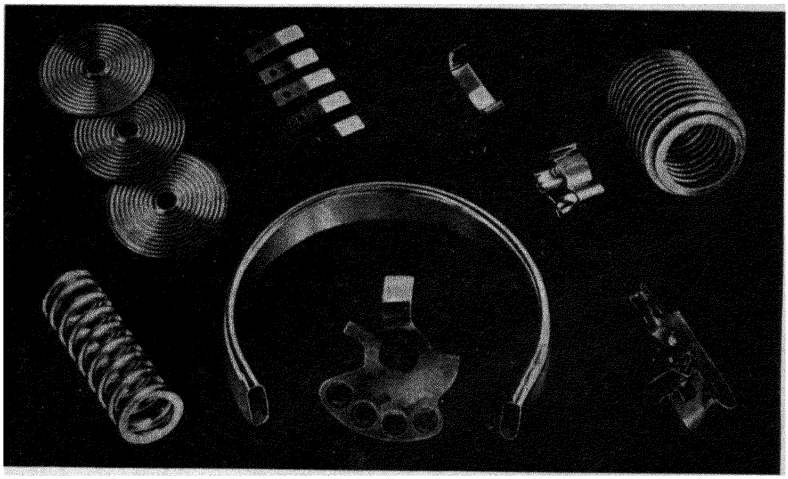

FIGURE 1
Products made of beryllium-copper alloys (courtesy of Beryllium Corporation of Pennsylvania).

Other Uses of Beryllium

Beryllium has recently been used in England as an ingredient of a new textile fiber, of the rayon type, made principally of seaweed. The solution for the new fibers is that of sodium alginate obtained from seaweed. They are spun by the usual machinery, i.e., a gear pump, a candle filter, made of diatomaceous earth or porcelain, a multiple-orifice jet (see chapter 7), and a final silk-fabric filter.

The quality of the yarn is a function of the coagulating bath.

A simple calcium chloride solution, which has been slightly acidified, is used, although the calcium alginate yarn tends to dissolve when washed with soap or the other alkaline agents used in laundries.[12] Improved washability is obtained by treating the yarn with aluminum or chromium acetate, but the best yarn so far obtained is that hardened in a bath of beryllium acetate. With increasing evidence of the feasibility of beryllium alginate yarn, the interest in beryllium compounds grows.

The transparency of beryllium metal to X-rays has been previously noted. Although pure beryllium is still a relatively expensive laboratory curiosity, the metal can be cast and ground into plates for the windows of large pieces of X-ray equipment, and it can be used for experiments in nuclear physics, for example, in special apparatus such as the cyclotron, where a metal of low density is essential. The several-million-volt X-ray apparatus figuring so prominently in medicine uses windows of pure beryllium when "soft" radiations are required.

Beryllium Oxide

Besides serving as the direct raw material for the arc furnace method of making beryllium-copper alloy, beryllium oxide, because of its very high melting point, 2570°C (about 300° above that of alumina), has been investigated as a refractory material.[17] It is very hard and has good insulating properties even at temperatures near its melting point. At these temperatures there is no sign of evaporation or of reduction by the furnace gases. Although beryllium oxide is attacked by acids it is more resistant to acids than is magnesium oxide. It is more basic than aluminum oxide.

Beryllium oxide is made from beryl by reacting it with acid sodium fluoride, leaching with hot water, and precipitating beryllium hydroxide, which is ignited to the oxide, BeO.

A rather unusual application of beryllium oxide is that devised by Price and Thomas[18] for the protection of silver articles against tarnish. The object is suspended as the cathode

in a solution containing 3.4 g/l of beryllium sulfate, $BeSO_4 \cdot 4H_2O$, and 1.3 to 2.3 g/l of ammonia, NH_3; the cathode current density is 46 milliamperes per square foot; the voltage is 7.5, and the planting time is 0.25 to 1.25 hours. The beryllium hydroxide produced at the cathode is electrophoretically deposited on the silver surface. Upon exposure to air, a film of BeO is formed which protects the silver against tarnish.

Beryllium Silicates

The silicates of beryllium have recently come into prominence as phosphor bases for the lining of fluorescent lighting tubes. Instrumental in the development of zinc beryllium silicate phosphors is Fonda of the General Electric Company Laboratories. Complex beryllium phosphors, activated with manganese or other elements, have been investigated by Leverenz and others. The success of our modern fluorescent lighting unit, as well as the television screen, has been due largely to the efforts of these researchers.[19]

Analysis

The chemistry of beryllium is similar to that of aluminum. A sufficient distinction between the two is afforded by reaction with a saturated solution of sodium acid carbonate, which dissolves the beryllium hydroxide precipitate but not that of aluminum. Quantitative separation of beryllium from aluminum is effected by 8-hydroxy quinoline.[20]

Ore Assay

The most generally successful assay method is that of Copaux.[21] Finely powdered beryllium ore is intimately mixed with twice its weight of sodium silicofluoride (a cheap by-product of the phosphate fertilizer industry). The mixture is heated for several hours at 850°C until the evolution of silicon fluoride has ceased, indicating the elimination of the silica constituent of the ore. The sintered material is then broken up

and leached for several hours with boiling water. The residue, composed principally of aluminum fluoride, remains on the filter. The filtrate is boiled down to a small volume; concentrated sulfuric acid is added, and boiling is continued until the vapors evolved are free from hydrofluoric acid. Upon dilution, the sulfates of calcium, strontium and barium are precipitated, the beryllium sulfate remaining in solution. Iron is removed from the solution with ammonia, and finally, pure $BeSO_4.4H_2O$ crystallizes out. It is then converted into beryllium hydroxide, which is ignited to the oxide and weighed.

Microchemical Tests

Several microchemical tests for beryllium have been developed and used with varying degrees of success. For example, a drop of uranyl acetate solution containing a trace of sodium is mixed by means of a platinum wire with a drop of the solution to be tested, and the mixture evaporated. In the presence of beryllium, pale yellow rhombohedral crystals form. This test is sensitive to 70.6 gammas.

A test ten times as delicate, detecting 7.6 gammas of beryllium, is the formation of beryllium acetyl acetonate. A solution of beryllium acetate is slightly acidified with acetic acid and treated with acetyl acetone. Monoclinic tablets or thin prisms are obtained on slow evaporation. With proper care, beryllium in an ore sample may be converted to the acetate, and this test applied.[22]

Beryllium compounds may be detected by the orange-red coloration produced by the addition of a yellow alkaline solution of *p*-nitrophenyl azoresorcinol.[23] Kolthoff [24] proposed and used a test for beryllium in which 0.1 cc of an ethanol solution of 1,2,5,8-hydroxy anthraquinone is added to 10 cc of the solution to be tested, together with 6 or 7 drops of 4 N ammonium hydroxide. After boiling and allowing to stand for 5 minutes, a red to orange-red precipitate forms.

Fluorochemical Tests

Beryllium may be detected in minerals by the Zermatten test,[25] based upon a fluorochemical procedure. The sample is fused with sodium carbonate, the melt dissolved in 5 N hydrochloric acid, and tetrahydroxy flavanol and sodium hydroxide are added. A yellow-green fluorescence in long wavelength ultraviolet light indicates the presence of beryllium.

In the test of Satch, the blue fluorescing nitride of beryllium is produced by passing ammonia gas for 4 hours over beryllium containing 10 per cent aluminum oxide at 1000°C. The only other appreciably fluorescent nitrides are those of aluminum and boron, but both of these require activation by silicon and carbon. Solutions of beryllium chloride, on the other hand, present a bluish fluorescence under long wavelength ultraviolet radiation,[26] and De Ment [27] has shown that solid beryllium chloride usually fluoresces feebly violet under long wavelength ultraviolet light, i.e., 3650Å. When a solution of beryllium chloride is mixed with tincture of alkanna, a bright orange-red fluorescence is seen when the mixture is excited with long wavelength ultraviolet light.[28]

An alkaline, violet solution of quinalizarin turns blue in an alkaline beryllium solution. With this reagent beryllium can be detected in the presence of aluminum and small amounts of iron, phosphates, and tartrates. Quinalizarin is also applicable for the colorimetric determination of beryllium.[29] In another test, 30 drops of a 0.05 per cent quinalizarin solution in ethanol are mixed with 5 drops of 10 per cent ethylene diamine, then a few drops of this reagent are added to a few drops of the unknown solution. The violet color turns blue if beryllium is present.[30]

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CHAPTER II

GALLIUM, INDIUM, AND THALLIUM

Introduction

There are five elements which make up what is known as the boron-aluminum family. The three elements treated in this chapter are the lesser known and comparatively scarce metals, gallium, indium, and thallium. All the elements in the boron-aluminum family bear a close resemblance to one another, and all are metals with the exception of boron, in which the non-metallic properties predominate.

It will be noted in table 2 that the physical properties of boron, aluminum, gallium, indium, and thallium increase with an increase in atomic weight. The basic properties increase and, correspondingly, acidity decreases with increasing atomic weights until thallium is reached. When trivalent, thallium behaves like the other members of the family, but when monovalent, it is more like silver and the alkali metals.

The exact classification of these metals, with their relationship to rare earths, has occasioned some difficulty but it is generally agreed at present that gallium, indium, and thallium are

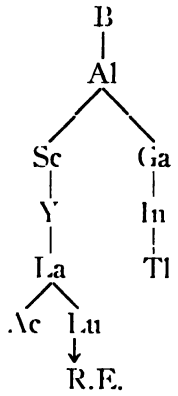
TABLE 2

PHYSICAL PROPERTIES OF BORON-ALUMINUM FAMILY METALS

Property	*Boron*	*Aluminum*	*Gallium*	*Indium*	*Thallium*
Atomic weight	10.82	26.97	69.72	114.76	204.39
Atomic volume	4.5	10.0	11.8	15.5	17.3
Specific gravity	2.45	2.7	5.9	7.3	11.85
Melting point, °C	2300	660	29.75	155	302.5
Boiling point, °C	2550	1800	1700	1450	1650

best grouped with boron and aluminum. However, the three rare elements, scandium, yttrium, and lanthanum are all related to the boron-aluminum family. They are all trivalent, just as most of the members of this family. Scandium, yttrium, and lanthanum were once classed with the rare earths and although they do closely resemble these elements it has recently been found more expedient to group them with gallium, indium, and thallium in the boron-aluminum family.

The chemical and physical properties of thallium are similar to those of the rare earths. This class of elements lies below thallium, scandium, and yttrium, as shown in the following diagram.



Scheme of the boron-aluminum family showing the position of gallium, indium, and thallium

Gallium

History

The discovery of gallium was the result of the early research of Boisbaudran in spectroscopic analysis. He observed that the spectral lines of the incandescent vapor of elements of the aluminum family form patterns of the same general type, showing regular variations from one element to the next. He

found a gap in the symmetry, between the spectra of indium and aluminum, which could be filled by the spectrum of a hypothetical element having properties intermediate between those of indium and aluminum.

With the spectroscope he searched for the missing element in 1863, but conditions were unfavorable for its discovery. In the autumn of 1868, he collected some zinc blende at Pierrefitte in the Pyrenees and renewed his efforts. In 1874, his investigations were successful, and the existence of the new element was announced. *Gallium* was the name chosen for the new element in honor of the discoverer's native country, Gallia being the Latin name of France. Boisbaudran succeeded in 1875 in electrodepositing the metal on a platinum cathode from an ammoniacal gallium sulfate bath.

Boisbaudran ascribed definite properties to the new element, but he hesitated to publish his views. Meanwhile, Mendeleeff was developing the periodic table and, publicly predicted with great accuracy, in 1869, the properties of the element located below aluminum in the periodic table, which he called *eka-aluminum*.

Mineralogy

Gallium is one of the scarcest elements. It is distributed very widely, but in minute amounts (5 parts per million), rarely occurring in large concentrations in any one ore or mineral. The most prominent sources of gallium are the zinc blendes, the richest ores being those mined in Germany. The black blendes of Cumberland contain gallium, as do those obtained from other localities, such as Pierrefitte (France), Saxony, Mandesse, Asturien, Rio Tuerto (Spain), and parts of Sweden. The Pierrefitte blende contains from 0.0014 to 0.0022 g of gallium per kilogram of ore. Bensberg black blende contains larger amounts, sometimes slightly exceeding 0.016 g of gallium per kilogram.

Gallium is rated as forty-seventh in abundance. In the ten-

mile crust of hydrosphere and lithosphere, Clarke and Washington [1] have estimated that it is present in amounts of about 10^{-5} per cent, and in igneous rocks the average amount of gallium present has been estimated as 10^{-11} per cent.

The presence of gallium has been noted in waste muds from the electrolytic processing and refining of various metals, and in the residue and flue-dusts from industrial distillations of volatile metals. It is present in the residues after zinc distillation in amounts that may range up to 0.002 g of the element per 10 kg of zinc, or about 1 part in 5,000,000. It is found in these residues as a mercury-like alloy with about 10 per cent its own weight of indium.

One of the richest natural sources of gallium is germanite, some specimens of which have been reported to contain as much as 0.5 per cent of the element.[2] It is also found in the sun, and meteorites contain traces (5 parts per million) of gallium.[3] Astrophysicists state that the spectrum of gallium may also be noted in the light of distant stars. Mineral waters and some sea water contain gallium in extremely small amounts.[4]

The spectroscope has shown that traces of gallium exist in many common ores. For example, the presence of gallium was established in 35 out of 91 iron ores,[5] in all 7 magnetites studied, in all 15 aluminum ores, in many specimens of kaolinite and bauxite, in 4 out of 12 manganese ores, and in 12 out of 14 zinc blendes. Facts such as these are extremely important when industrial applications of gallium are considered.

The concentration of gallium was determined in mineral samples collected by the expedition from the Lomonosof Institute of the Academy of U.S.S.R. The estimation of gallium was made spectroscopically and the results are shown in table 3.[6]

TABLE 3

GALLIUM IN MINERALS [6]

Mineral or Rock	*Locality*	*Per Cent Gallium*
Germanite	Tsumeb, South Africa	0.7
Blendes	Pyrenees	0.15–0.23
Muscovite	Turkestan	0.01
Pegmatites	Turkestan	0.001–0.01
Lepidolite	—	0.001
Phlogophite	Dudianka, Siberia	0.01
Pegmatite-feldspars	Altin-Toou	0.001–0.01
Corundellite	Turkestan	0.0001
Beryl	Altin-Toou	0.01
Zinc spinel	Altin-Toou	0.01
Zinc blendes	Kinibing	0.001
Zinc galena	Kirghisie	0.0001
Iron minerals	—	< 0.0001

Physical Properties

Pure metallic gallium, of atomic weight 69.72, is a grayish, mercury-like crystalline solid of low malleability. It melts when held between the fingers. Its melting point is just under 30°C and its boiling point is 2300°C; thus there is a remarkably large difference between melting and boiling points.

The most accurate determinations of its specific gravity were made by Richards and Boyer,[7] who found a value of 5.907 for solid gallium and 6.081 for liquid gallium. The values determined by various investigators differ slightly. The specific heat of gallium is 0.0926 at 16 to 24°C, and its latent heat of fusion is 18.5 cal per g.[8] Liquid gallium is electro-negative to the solid element.

One of the outstanding characteristics of gallium is its spectrum. The spark spectrum first observed by Boisbaudran has two violet lines at 4172.2 and 4033.18Å, the former line more intense than the latter. The flame spectrum of gallium, unlike the spark spectrum, is feeble and quickly fades. Three other lines may be seen with the eye in the visible spectrum, although these are comparatively weak. The lines lie at wavelengths

6396.99, 6413.92, and 3020.61Å. Spectral analysis of gallium is best performed by spectrographic means, but for routine tests and rapid surveys of material a small hand spectroscope may be employed to advantage.

Gallium is diamagnetic and has an atomic refraction of about 14.8.[9] Its electrical resistivity is $53.4^{\times 10^{-6}}$ at 0°C.[10] The element forms many alloys, which have been studied extensively. These will be discussed presently, but it is pointed out that gallium alloyed with other metals, such as tin, gold, etc., possesses very unique properties.

A globule of molten gallium may be kept in the fluid state indefinitely, but upon contact with a foreign object, it will instantly solidify to a crystalline mass.

Gallium may be prepared in the form of large single crystals which are useful for scientific studies. Single crystals of the metal many centimeters in length can be prepared by the Taylor process, in which the metal is fused and drawn while contained in a fine glass capillary.

Chemical Properties

Pure gallium preserves its luster in air and is not affected greatly by acidic fumes. Air at red heat oxidizes the metal superficially. Metallic gallium does not emit occluded gas when heated in a vacuum.

Dry oxygen at 285°C exerts no visible action on gallium. However, at incipient redness gallium loses its luster and becomes covered by a thin grayish-blue pellicle; at full red heat a distinct oxide film forms. This film protects the metal from further oxidation, as in the case of aluminum. When gallium is heated to bright red heat, a slight sublimation of the oxide takes place.

Gallium remains bright in air-free, boiling water. However, it does oxidize slowly in boiling water which contains dissolved air. When crystalline gallium, prepared by electrodeposition, is thrown into hot water it crackles and bubbles, with the escape

of gas, probably hydrogen occluded during electrodeposition (cf. first paragraph). The hydride of gallium is formed at a temperature of 170°C.

Compounds

Gallium unites with chlorine, bromine, and iodine at ordinary temperatures, in a decreasing order of activity. It is slowly dissolved by concentrated hydrochloric acid, either cold or hot, with a gradual evolution of hydrogen gas. The action of acids is faster on solid gallium than on the liquefied element. It is slowly dissolved by cold nitric acid, more quickly by the hot acid. Aqua regia is a good solvent for gallium, but even with this reagent the action is not rapid.

Gallium dissolves in potassium hydroxide solution with the evolution of hydrogen. Gallium is ordinarily trivalent but it may also exhibit a valence of two in the gallous compounds. The gallous salts are unstable and reduce many substances. Electrochemically, gallium is nobler than zinc but less noble than iridium.

As previously mentioned, gallium forms alloys with many metals. Cadmium, zinc, aluminum, tin, mercury, and others combine with it at room temperatures. A gallium-aluminum alloy containing 2.54 per cent aluminum is liquid at room temperatures (20°C). Gallium also alloys with copper, platinum, silver, and iron.

Extraction from Ores

To extract gallium from germanite and gallium-bearing zinc blendes, the mineral is dissolved in aqua regia and the excess acid boiled off. When the solution is cold, zinc metal is added, causing precipitation of arsenic, antimony, bismuth, copper, cadmium, gold, lead, silver, mercury, tin, selenium, tellurium, and indium.

The precipitated metals are filtered off while hydrogen is still being evolved and the filtrate boiled for a period of from 6 to

24 hours with metallic zinc. Gallium is precipitated as a basic salt, together with the salts of aluminum, iron, and others. To obtain the pure gallium salt, the precipitate is dissolved in concentrated hydrochloric acid and the solution saturated with hydrogen sulfide. Gallium remains in solution. After filtering, the excess hydrogen sulfide is removed from the solution by boiling.

Finally, sodium carbonate is added to the filtrate in small amounts for fractional precipitation. The gallium precipitates first and the precipitates are collected as long as they show characteristic gallium lines in the spark spectrum. These precipitates are dissolved in concentrated sulfuric acid and the solution boiled after dilution with water. The basic sulfate of gallium which comes out of solution is dissolved in sulfuric acid and potassium hydroxide is added in excess. Any iron present is removed at this point in the filtration. The gallium oxide is then precipitated from the filtrate either by passing carbon dioxide into the solution or by adding a small amount of easily obtainable solid carbon dioxide.[11]

Technology

At present, the commercial applications of gallium are few. Many reports have been accumulated as to the distribution and abundance of gallium in minerals, flue-dusts, and waste by-products from various metallurgical processes, notably zinc and copper processes. However, demand for this metal has not yet exceeded the supply, but continued search for its uses should be encouraged.

Since gallium has a low melting point and a relatively high boiling point, it has been employed in high temperature thermometers. Gallium thermometers made from quartz allow measurement of temperatures far exceeding those measurable by the ordinary mercury devices. The low melting point of gallium alloys may lead to an application in fire-alarm systems.

Gallium is non-poisonous and has been used to a slight extent

in dental alloys. The studies which have been made so far indicate that it has superior workability and corrosion resistance.

Gallium has found some use as an excitant in phosphors for fluorescent lighting and luminous paints. The consumption of gallium for this purpose is as yet very small.

Gallium adheres easily to glass, forming a bright silvery film. This property may someday lead to a new use for gallium.

Analysis

In routine tests of minerals and residues for gallium, 10 g of the solid, such as blende, are dissolved in aqua regia and the excess acid expelled by boiling. Pure zinc is introduced into the solution and the precipitate filtered off while hydrogen is still being evolved. The filtrate is boiled with zinc and the precipitate that forms is first washed with water and then dissolved in hydrochloric acid. This solution is tested spectroscopically, since any gallium that was originally present is concentrated by this treatment.

Another qualitative determination of gallium [12] is based on the fact that metallic zinc readily removes 0.16 mg of gallium from a liter of solution, even in the presence of many foreign substances. The only drawback of this method is the difficulty of obtaining sufficiently pure zinc Electrolytically refined zinc or zinc purified by distillation should suffice. Metallic copper, copper hydroxide, and copper oxide may be used in place of zinc for the analysis.

In the gravimetric determination of gallium the metal is isolated and weighed. This is accomplished by subjecting an alkaline solution of the oxide to electrolysis at a current density of 6 amp per square centimeter on a copper (*not* platinum) cathode. The electrolyte containing the gallium may be tested spectroscopically to insure complete removal of the element. Should the spectroscope reveal the presence of two violet lines at 4171 and 4031Å electrolytic processing should be continued.

Gallium forms a light red lake with an alcoholic solution of

alizarin in the presence of ammonia and ammonium chloride. This reaction may be employed as a test for the element. When used under favorable conditions it will enable the analyst to detect 1 gamma of gallium in 2 cc of diluent. The gallium, however, should be separated from interfering ions.[13]

Another test for gallium is the addition of 1 cc of the neutral or weakly acid solution to be tested to 3 cc of 0.5 per cent manganese chloride solution in 6 to 7 N hydrochloric acid, and 5 drops of 1 N potassium ferrocyanide containing in each 20 cc of solution 10 drops of a 1 N potassium bromide solution. In the presence of gallium a reddish-brown precipitate or turbidity is developed.

In detecting gallium fluorochemically, the solution to be tested is mixed with sodium fluoride until about 8 per cent has been added. The appearance of a green fluorescence when morin reagent is added indicates the presence of gallium. The sodium fluoride inhibits the action of any aluminum that may be present.[11]

Indium

History

The discoveries of gallium, indium, and thallium all have one thing in common: they were discovered by the spectroscope. Characteristic, brightly colored, and comparatively simple spectra were observed in the visual range.

Indium was discovered in 1863, 2 years after the discovery of thallium, by Reich and Richter, who were examining a sphalerite ore from Freiberg with the spectroscope. The ore consisted chiefly of sphalerite, galena, and arsenopyrite. It was first roasted to expel sulfur and arsenic, then treated with hydrochloric acid and evaporated to dryness. The crude chloride of zinc thus obtained was examined with the spectroscope for thallium, since the presence of this element had just been established and researchers throughout the world were endeavoring to establish its presence in various substances.

Instead of finding thallium and observing the bright green line of its spectrum, Reich and Richter noted prominent indigo blue lines which had never been observed before. Realizing that a new element might be present they concentrated their sample and soon found the new element, which they named *indium* after the color of its spectral lines.[15]

Mineralogy

Indium is often found in minute amounts in zinc minerals, especially sphalerite. Certain zinc and lead ores of Mohave County, Arizona, contain relatively large amounts of indium.[15] The pegmatite dikes of western Utah also contain abnormally large amounts of indium, in fact, Romeyn [16] has reported that these rocks may contain up to 2.8 per cent indium and 1.2 per cent scandium. Indium is found associated with cadmium, thallium, and gallium. It is also recovered as a by-product in the lithopone industry.[17] Complex lead ores have been reported to contain as much as 2 oz of indium per ton.[18]

Indium can be recovered from the spelter of indium-containing zinc sulfides by treating the spelter with sulfuric acid. The residue obtained from this treatment usually contains the greater part of the indium originally present.

Tungsten ores, such as wolframite from Zinnwald, contain indium. Usually the amount of indium in ores is from 0.1 per cent to mere traces, but as pointed out above, exceptional cases exist in which the element may be present in relatively large concentrations. Some manganese ores, tin ores, and many of the iron ores, such as siderites, have been shown spectroscopically to contain traces of indium. The presence of indium in the sun was established by Lockyer.

Physical Properties

Indium is a metal which looks very much like tin, being silvery-white in color with a slight bluish tinge. Just as in the case of tin, a bar of indium emits the "cry" when bent. It is malleable, softer than lead, and may be drawn into wire. Its

melting point is 156.4°C and its boiling point is 1350°C.

The atomic weight of indium is 114.76 and its atomic number is 49. It does not have more than two isotopes because its atomic number is odd. The isotopes of indium, which have been shown to exist, are those with an atomic mass of 115, present in ordinary indium to about 95.5 per cent, and an isotope of mass 133, which makes up the remaining 4.5 per cent.

Indium readily marks paper. It colors a non-luminous flame bluish-red and gives a flame spectrum consisting of two principal lines, one at 4511.55Å and the other at 4101.95Å These are violet and may be mistaken for the violet potassium line which lies nearby. The 4101.95Å line is visible only in the spectrum of rich specimens, as are a number of other indium lines in the indigo, near-ultraviolet, and short ultraviolet regions.

Considerable work has been done by Ludwick in compiling literature references on indium. His bibliography is a continuation and extension of efforts by Ekeley and Potratz,[10] who covered the literature between 1863 and 1933. Ludwick's work includes citations from 1934 to the present time.[20]

TABLE 4

PHYSICAL PROPERTIES OF INDIUM

Property	*Value*
Atomic weight	114.76
Atomic number	49.
Isotopes	Mass 115 = 95.5% Mass 113 = 4.5%
Valences	Commonly 3, also 2 and 1
Atomic volume	15.5
Melting point	155°C
Boiling point	1450°C
Specific gravity	7.31
Specific heat	27.3 joules per gram-atom
Resistivity at 20°C	9 x 10^{-6} ohm-centimeter
Thermal expansion at 20°C	33 x 10^{-6} per °C
Brinell hardness	1
Tensile strength	15,980 lb. per sq. in.
Crystal system	Tetragonal
Normal electrode potential	–0.336 volt
Heat of ionization → In^{+++}	–32.7 cal

Chemical Properties

At ordinary temperatures pure indium metal is stable in air, but on heating in oxygen it burns with a blue flame to the trioxide, In_2O_3. Indium retains its luster when immersed in boiling water, but dissolves slowly in hydrochloric and sulfuric acids, more readily in concentrated nitric acid.

Compounds

Chemically, indium resembles zinc in some respects and aluminum and iron in others. Indium is trivalent in its stable compounds. It also acts as a bivalent metal and, more rarely, as a monovalent metal. Like the sulfates of aluminum and gallium, indium sulfate forms alums with monovalent metal sulfates.

When indium dissolves in sulfuric acid the sulfate is formed, with an accompanying evolution of hydrogen. In hot concentrated sulfuric acid, sulfur dioxide is evolved, and in concentrated hydrochloric acid the soluble trichloride forms with the evolution of hydrogen. When it dissolves in nitric acid, nitric oxide is given off, and ammonia is formed from the reduction of nitric acid. Oxalic acid dissolves indium with the formation of an oxalate, but acetic acid does not affect it.

Extraction from Ores

One method [12] for extracting indium from indium-containing sphalerite is carried out by first roasting the mineral thoroughly, boiling the residue with dilute sulfuric acid, filtering, and nearly neutralizing the filtrate with sodium carbonate, then placing clean plates of zinc in the solution. The precipitate formed on the plates is removed from time to time.

To isolate the indium, the zinc is dissolved in dilute sulfuric or hydrochloric acid and boiled until the evolution of gas ceases. When the precaution is taken to leave a little zinc undissolved, the metallic precipitate remaining contains all the indium pres-

ent together with the zinc. The residue is then dissolved in nitric acid and the indium precipitated from the cold solution as the oxide with barium carbonate. The oxide is reduced to the metal by heating in a stream of hydrogen.

The oxide is an important source for other indium compounds. Conversely, it may be prepared by ignition from its salts, such as the carbonate, nitrate, or sulfite. Pure indium trioxide exists in two modifications. One, which is yellow and non-crystalline, is soluble in acids. The other, a grayish-white modification, is very resistant to acids, forming trigonal crystals, and is prepared by ignition at high temperatures. Boiling with dilute sulfuric acid is a good means for separating the two modifications.

Preparation of the Metal

Elemental indium may be obtained by several methods. The oxide may be reduced with carbon or heated in a stream of hydrogen. Soluble indium salts precipitate metallic indium when an excess of zinc is added. The sulfate may be electrolyzed and pure indium deposited on the cathode.

Since indium is a scarce and valuable metal, means are frequently taken to recover it from waste liquors in electroplating and other operations. A very good method has been worked out by Dyer of the Indium Corporation of America. It entails the evaporation of the liquor to dryness to eliminate water and then destroying organic materials by ignition at about 700°C under good draft hoods. Silver, mica, and a little lead are eliminated by dissolving the residue in hydrochloric acid, filtering, and washing with cold water. Silver chloride, silica, and a small amount of lead chloride remain on the filter. Remaining impurities and indium are contained in the filtrate.

Copper, cadmium, zinc, and nickel are separated from indium, iron, and tin by precipitating from solution with an excess of ammonium hydroxide, filtering, and washing with dilute am-

monium hydroxide. The filter retains indium, iron and tin hydroxides. The filtrate, containing copper, cadmium, and zinc in solution, is discarded.

The combined indium, iron, and tin hydroxides are dissolved in a strong solution of hydrochloric acid and the solution subjected to a plating current of about 7.5 v. The cathode will collect all of the indium and traces of iron, tin, and nickel. This cathode is then made the anode in a sulfuric acid bath and pure indium plates out. Tin, nickel, and iron remain in solution whereas the indium plated out will be of relatively high purity, containing at most only a trace of iron.

Technology

Like many other rarer metals, indium has until recently been nothing but a laboratory curiosity. Before 1924 it was extremely difficult to obtain metallic indium in sizeable amounts. The growth of the indium industry and the rising general interest in indium is partly due to the efforts of William S. Murray. Murray, many years ago a researcher on rare elements, turned toward indium for new metallurgical developments.

Murray encountered many difficulties trying to get an appreciable amount of pure indium to work with, and only after placing his order with a New York chemical concern for several months was he able to get 1 g of the element. The gram of indium was gathered together from various sources and cost considerably more than an equal weight of platinum. However, it was soon demonstrated that indium was valuable for increasing corrosion resistance and for stabilizing non-ferrous metals.[21]

At the present time, indium can be obtained at prices which range from approximately one-third the price of gold, per troy ounce, to slightly lower values. The price of indium is gradually decreasing with the increasing use of the metal. Indium can be used in bearings, packing material, jewelry, fluorescent glass,

collapsible tubes, molds for plastics, contact points, light reflectors, etc.

Diffusion of Indium

Some of the most promising applications of indium are in the field of plating. Indium possesses a unique advantage, in that it can be diffused, after plating, by a low-temperature heat treatment. This plating and diffusion process may be regarded as an actual alloying of the indium with the base metal. In any event, the indium after diffusion becomes a part of the surface and hence offers a higher degree of immunity to chipping or peeling than is the case with most electro-plated finishes. When applied in this manner, indium greatly increases the corrosion resistance of the metal.[22]

Indium Plating

With the increasing realization that indium plate and indium which has been heat-diffused into the surface of a base metal can be of utmost importance in many industrial fields, there is more demand for details about the electrodeposition procedure.

Indium plating from basic cyanide solutions has been studied by Murray [23] and Gray.[24] The baths they used consisted of indium sodium cyanide stabilized with a weakly acidic organic compound, such as d-glucose. Under constant use such electrolytes tend to break down and become unsatisfactory.

The electrodeposition of indium from sulfate baths was studied by Fink and Lester,[26] who concluded that since sulfate solutions are very stable they offer the best possibilities for indium plating. In this study insoluble anodes were employed in a solution which was changing continuously during the plating operation. The addition of either boric acid or aluminum sulfate to the solution was recommended. The boric acid acts as a buffer. The aluminum sulfate has practically no effect on the solution as a whole, acting only at the cathode surface.

Indium plating has also been studied by Linford,[25] who employed indium sulfate as the electrolyte for producing smooth matte surface deposits. The thickness of such a coating is of the order of 0.0025 mm. An indium sulfate plating bath has proved superior to many others, since it is stable and constant in performance when the pH is regulated. Linford's method uses a combination of soluble and insoluble anodes for maintaining a constant pH value of from 2.0 to 2.7.

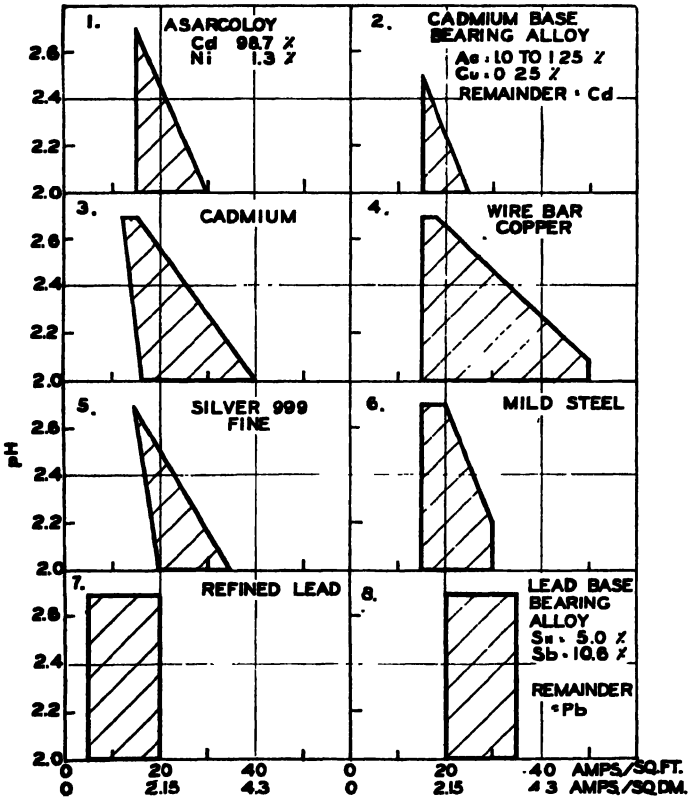


FIGURE 2.

Indium plating on base metals [Linford, *Trans. Electrochem. Soc.*, 79, 443 (1941)]

The diagrams show the range of pH and current density for indium plating on various base metals at 20°C, with solution containing 20 g/l of indium sulfate.

Alloys

One of the first uses for indium was in certain dental alloys. The addition of 0.5 to 5 per cent indium greatly improved the corrosion resistance, hardness, and strength of the alloys. Indium has also been made into hinge pins for spectacle frames because of its resistance to corrosion.

Silver-indium alloys have been developed which contain from 1 to 25 per cent indium. They are employed as a tarnish-resistant plating silverware. It has been pointed out that 42 per cent indium is required in silver to prevent tarnishing by alkali sulfides. Silver alloys containing over 40 per cent indium are hard, brittle and difficult to work. For certain uses these silver-indium alloys are not practical. In plating base metals, a coating of silver is first applied, and then the indium. The indium-plated ware is then heat-treated to diffuse the indium. Such a plated surface takes a high polish.

One of the latest applications of indium is for protection of bearings against wear and corrosion in internal combustion engines. Indium has been especially effective in airplane manufacture; it has recently been reported that a thin layer of indium, electroplated and heat-diffused into cadmium-silver-copper automobile bearings, prevents high-temperature corrosion from the acids in petroleum lubricants. Indium combined with non-ferrous metals has properties similar to those of chromnium combined with the ferrous metals, i.e., it is resistant to oxidation, permits a high polish and has a high tensile strength.[27]

Wood's metal can be alloyed with indium to produce a low-melting metal. When about 18 per cent indium is employed, the resulting alloy melts at 46.5°C and is useful as a molding material. Other low-melting alloys can be alloyed with indium since this metal further reduces the fusing temperature. Indium should be very useful for producing alloys which find application in sprinkler systems and other fire-protection devices.

Dental amalgam may be obtained by combining indium with mercury. Usually about 95 per cent mercury is used with about

5 per cent indium. Indium possesses several desirable characteristics. The presence of indium does not interfere with dental requirements, such as susceptibility to carving for a limited time, absence of granular consistency, and susceptibility to receiving and retaining a polish. Since indium costs only about one-third the price of gold, and considerably less than the price of the platinum metals, research in the dental alloy field may be well worth while.

Many of the alloys used in jewelry can well be modified to include indium for a reduction in price without sacrificing beauty. The gold, silver, platinum, and palladium alloys of indium already developed can be used in jewelry, watch cases, etc. Indium is soft, heavy, and has a silvery luster, like the other precious metals used for adornment.

Indium added to copper makes it corrosion- and wear-resistant. It also forms alloys with the ferrous metals.

Other Uses

The oxide of indium can be used to color glass from a light to a dark yellow shade depending on the amount added. It is claimed that 1 part indium trioxide in 2000 parts glass will impart a beautiful yellow coloration. Such glasses may also be had with a bright fluorescence after proper treatment.

The tarnish-resistance of indium coupled with its high reflectivity make possible its application in the field of optics. Indium can easily be sputtered and plated on glass. It can be used as a reflector metal on surfaces which must withstand fairly high temperatures; in this case the layer would probably be partly diffused into the base metal.

There is no reason why indium cannot be burned into ceramic ware and dishes by using an indium-containing paint (like the platinum metal paints) and an organic base. In this case, the indium paint would be applied on the surface and the article subjected to heat treatment. The organic base would leave the indium intact on the glass or porcelain surface.

When it is remembered that as recently as 1924, several months' work was required to obtain even 1 g of indium, it will be realized that the industrial history of this metal has been very short. In view of its early stage of development and its unique properties, it is evident that existing applications represent only a small fraction of its future possibilities.

The familiar cycle of industrial development of any commodity takes the following course. Research makes possible cost reduction and points the way for applications. Increasing demand created by these results makes possible still further cost reductions. Continued and stabilized demand establish the metal or commodity as one of permanent significance. This is exactly the case for indium, although as yet it is only in the developmental stages, with an unpredictable, but fairly bright future in industry.

Analysis

Because of its characteristic indigo spectrum, indium can be detected qualitatively in residues and concentrates with the spectroscope. Using spark and hot cathode layer methods of spectral analysis, it is possible to detect as little as 1 gamma of this element. There are also a number of microchemical tests for indium. Usually cesium compounds are used to obtain characteristic crystals of indium salts, although some organic reageants, such as methanamine, have been proposed and used at different times.

Residue Assay

Lawrence and Westbrook [17] have developed a method for analysis of indium in residues from zinc smelting operations. The procedure of these investigators is to take the process residue, which contains about 1 per cent indium when dry, and digest it with dilute sulfuric acid until it has dissolved, except for a small amount of lead sulfate, insoluble silicon dioxide, and some gangue.

After filtration, the solution is treated with zinc shavings until the iron has been reduced and nearly all the free acid eliminated. An excess of zinc shavings is added to the slightly acid solution, and the precipitated metals and shavings are filtered off and washed with hot water. The precipitated metals and shavings are then dissolved in dilute nitric acid, the resulting solution treated with a mixture of ammonium hydroxide and ammonium chloride, and boiled until only a faint odor of ammonia is noticed.

The precipitated hydroxides of indium, aluminum, iron, gallium, germanium and other elements are filtered off and washed with hot 2 to 3 per cent ammonium chloride solution and then dissolved in dilute hydrochloric acid. This procedure is repeated to remove most of the zinc, cadmium, and copper.

Additional separation from the heavy metals is accomplished by dissolving the hydroxides in dilute hydrochloric acid, regulating the acidity to 2 N, and saturating the solution with hydrogen sulfide. After the mixture is warmed to coagulate the precipitated sulfides of the group II elements, they are removed by filtration and washed with hydrogen sulfide water.

The filtrate is then boiled to expel excess hydrogen sulfide and treated with an excess of potassium hydroxide and boiled again. The resulting precipitate consists of indium hydroxide and a small quantity of ferric hydroxide. This is filtered, washed, and dissolved in acetic acid. After dilution with water and the addition of ammonium acetate, the indium is precipitated as the sulfide with hydrogen sulfide gas. The indium sulfide is filtered, washed, and then dissolved in hydrochloric acid and reprecipitated as the hydroxide, as before. The final precipitate of indium hydroxide is then ignited to indium trioxide in a tared porcelain crucible at about 700°C. The purity of this oxide may be determined spectographically and further purified if necessary.

Detection and Analysis

The reactions of a number of common chemical reageants with the salts of indium are given in table 5, since they may have an analytical application.[11]

TABLE 5

CHARACTERISTIC INDIUM REACTIONS [11]

Reagent	*Product*
Ammonium hydroxide	White gelatinous indium hydroxide insoluble in an excess of reagent.
Potassium hydroxide	White gelatinous indium hydroxide soluble in excess of reagent, and reprecipitated on boiling or with ammonium chloride.
Organic bases, e.g., piperidine, guanidine, and dimethylamine	Quantitative precipitation.
Hydroxylamine	Indium hydroxide.
Ammonium carbonate	Indium hydroxide soluble in excess reagent and reprecipitated on boiling.
Sodium carbonate	Indium carbonate insoluble in excess reagent.
Potassium ferrocyanide	White precipitate.
Potassium ferricyanide	No precipitate.
Potassium chromate	Yellow precipitate.
Potassium dichromate	No precipitate.
Hydrogen sulfide	Yellow indium sulfide from acidic or slightly neutral solutions.
Metallic zinc or cadmium	Metallic indium sponge.

The following is a convenient test for indium. Place 1 drop of the solution to be tested in a small porcelain crucible or dish and add saturated sodium thiosulfate solution drop by drop until no more violet coloration develops. Add a grain of sodium sulfite and 6 to 8 drops of 5 per cent potassium thiocyanate solution and place the entire solution on filter paper moistened with a saturated alizarin solution in ethanol. Then dip the filter paper into a saturated aqueous solution of boric acid. The presence of indium is indicated by the formation of a red coloration on the filter paper.[28]

Another test for indium is to evaporate the test solution

with sulfuric acid, take up the residue with water and add cesium chloride. If indium is present, colorless octahedral crystals will form. Ammonium fluoride may be substituted for the cesium salt. Interference is encountered from aluminum and iron and these two elements must be removed before the test is conducted.[29]

A sensitive test for indium, gallium and thallium is carried out by adding 1 cc of saturated ammonium chloride solution to 1 cc of a neutral solution of the substance to be tested, and introducing 5 drops or more of quinalizarin solution (0.5 g in 10 cc of ammonium hydroxide). Immediate precipitation takes place with as little as 0.7 gammas of indium, 8 gammas of gallium, and 100 gammas of thallium per cc of solution. If zinc and aluminum are present the sensitivity of the test for indium and gallium is decreased.[30]

Indium produces a whitish precipitate when a drop of the solution to be tested is added to a drop of a saturated solution of methanamine sulfate and a drop of a saturated solution of ammonium thiocyanate. Iron and zinc also produce a reaction, giving reddish crystals in the first and whitish precipitate in the latter case.[31]

Fluorochemical Tests

The fluorochemical analysis of indium has been described by the writers in earlier works.[32] Morin or tetrahydroxyflavanol is used to detect fractions of a gamma of the element. A characteristic fluorescence develops if aluminum, scandium or other elements do not interfere.[33]

Indium may be conveniently subjected to fluorescence electographic analysis. The procedure can easily be adapted for use on bars and lumps of indium to estimate and detect the presence of trace elements such as iron. The presence of small amounts of iron in indium, often an impurity, can be detected by its quenching action on fluorescent substances.[34]

Thallium

History

Crookes, whose name has figured so prominently in the discovery and basic investigation of several rare elements, discovered thallium in 1861 quite by accident. Crookes was examining the seleniferous deposit from the lead chambers of the sulfuric acid works of Tilkerode in the Hartz Mountains of Germany, where iron pyrites were used in the production of sulfuric acid.

These deposits were known to contain selenium, and residues, which remained in significant quantities after extraction of this element, were set aside and not studied until the year 1861. During this time Crookes needed tellurium for his studies and after several unsuccessful attempts to isolate the element from the residue, he resorted to spectroscopic analysis. On examining the mixture in the flame he noted that after the spectrum of selenium had faded away a bright green line flashed into view. This line did not belong to any of the known elements of that day, and on further investigation Crookes proved that it was due to a new element of the aluminum family.

Crookes named his new element *thallium*, from the Greek noun meaning *budding twig*. However, at about the same time an independent French researcher, Lamy, announced the discovery of the same element. A controversy ensued and after the evidence for both sides was weighed, it was decided that Crookes should have priority. Credit must be given to Lamy for preparing large amounts of pure thallium in bar form, although Crookes had previously isolated the metal.

Mineralogy

Thallium is found in several distinct mineral species, all of which are comparatively rare. It is not found native.

Crookesite, $(Cu, Tl, Ag)_2Se$, is a thallium mineral, containing

from 16 to 19 per cent of the element. Crookesite is a massive, compact mineral having a metallic luster and a specific gravity of 6.9. It was first obtained from the mine of Skrikerum in Sweden, but it has been found elsewhere since then. An important thallium mineral, lorandite, $TlAsS_2$, contains from 59 to 60 per cent of the element, and a complex species known as hutchinsonite, $(Tl,Ag,Cu)_2S(As_2S_3)_2.PbS$, contains from 18 to 25 per cent thallium.

Thallium is present as a minor constituent of berzelianite (copper selenide) in small amounts in many other ores, in spring waters and in sea water. It occurs in limited quantities in sylvite, carnalite, and in some varieties of iron, copper, zinc, and cadmium sulfides in which it is combined with sulfur.

Thallium may also be found in mica, lepidolite, calamine, metallic zinc, gallium, and indium, and in bismuth, mercury, and antimony ores. Native sulfur and many of the selenides and tellurides carry traces of thallium.

According to its valence state thallium may exist with cesium, potassium, and rubidium, all of which it closely resembles in some respects. Otherwise, it may resemble other members of the aluminum family and be found in their ores.

Thallium in Flue Dust

One of the richest sources of thallium is the flue dust from sulfuric acid manufacture, in which pyrites and other sulfides are roasted. The flue dusts from iron works and those obtained from other metallurgical operations also contain varying amounts of thallium. The extraction of thallium from flue dust by the Crookes method gives comparatively large yields of the element. For example, some flue dusts give as much as 80 lb of crude thallium chloride from 3 tons of dust (9%Tl).

Extraction

The original Crookes method for extracting metallic thallium or thallium compounds is still in use today with certain

modifications. According to the directions given by him, the flue dust containing thallium is mixed in porcelain or wood vats with an equal weight of boiling water, and after a thorough stirring, the nitrogen dioxide is allowed to pass off. This gas results from the use of nitric acid in the chamber process of making sulfuric acid. The mixture is allowed to stand for 24 hours so that the undissolved residue will settle to the bottom of the vessel.

The supernatant liquid is decanted and the residue washed and treated again with a fresh portion of boiling water. The collected liquids taken from the sediment are allowed to cool and are then treated.

Physical Properties

Metallic thallium is a market commodity. In appearance it is not unlike lead, with a blue-gray tinge which is best noted on a freshly cut surface. Pure thallium is almost as soft as sodium and may easily be cut with a knife or scratched with the fingernail. It has a low degree of tenacity and is quite malleable. The resemblance between metallic thallium and lead is quite close in a number of physical properties. For example, the specific gravities are not widely different; thallium has a specific gravity of 11.88, whereas lead has a specific gravity of 11.37. Thallium fuses at 302.5°C and lead at 327.4°C. Like lead it can be extruded. It also marks paper readily, forming a streak which is blue at first, gradually changing to a yellow color, and which, after several days of exposure to the air, fades away completely. Other physical data for thallium are to be found in table 2 in this chapter.

Chemical Properties

Pure thallium oxidizes rather quickly in air and in water containing dissolved air. Thallous hydroxide, TlOH, is formed during oxidation in the presence of water. When heated to redness, thallium metal decomposes water. Thallium dissolves

in nitric acid and in sulfuric acid with the formation of the corresponding salts, but it is only slightly affected by hydrochloric acid because of the insolubility of thallous chloride in water.

Compounds

Thallium has two valences, one and three. The thallous salts are most stable and are by far the most numerous, many investigations having been conducted upon them. The thallic compounds are not so well known. Oxidation of thallium in air results in the formation of the brownish thallous oxide, but if the reaction is carried out in pure oxygen, thallic oxide will be obtained. As would be expected, strong oxidizing agents convert thallous compounds into thallic salts and reducing agents have the opposite effect.

Thallium resembles a number of metals outside its immediate family.[ab] The close resemblance of the free metal to lead has already been pointed out. In its monovalent condition thallium may be compared to the alkali metals, silver, and mercurous mercury. The trivalent salts also show some resemblance to lead, aluminum, gallium and indium.

The thallous halides, for instance, like those of silver, are only slightly soluble in water. Mercurous, thallous, and silver chlorides are soluble in a solution of sodium thiosulfate. Thallous sulfide, like the silver and lead sulfide, is only sparingly soluble in water. Thallous hydroxide and thallous carbonate are fairly soluble in water. The thallic salts are not very stable and behave somewhat like auric salts, so that, while thallous oxide, Tl_2O, is a strong base, the trioxide, Tl_2O_3, is a feeble base. Frequently, the thallous salts are more stable than the thallic.

Crude thallous chloride precipitates out of solution with a large excess of hydrochloric acid.

This salt is removed by filtration, thoroughly washed, and allowed to dry. It may be purified further by adding small

portions of it to half its own weight of hot sulfuric acid in a porcelain vessel, stirring constantly and heating until all the hydrochloric acid and the excess sulfuric acid have been driven off. The fused thallium acid sulfate is then dissolved in an excess of water and a strong stream of hydrogen sulfide passed through the solution to precipitate the arsenic, silver, lead, bismuth, mercury, and antimony.

These sulfides are removed by filtration and the filtrate boiled until all the free sulfurous acid has been driven off. The liquid is then rendered alkaline by ammonium hydroxide and again heated to the boiling point. The precipitate of ferric and aluminum hydroxides which often appears at this stage of the extraction is removed by filtering and the clear filtrate evaporated to a small volume. On cooling, relatively pure thallium sulfate crystallizes out. It may be recrystallized for additional purity.

Preparation of the Metal

It is not difficult to obtain relatively pure thallium. There are several methods of preparation. If an alkaline solution of a thallous salt is treated with zinc, the thallium is thrown out as an insoluble, fine, grainy precipitate and the zinc goes into solution. It is also possible to prepare metallic thallium by fusing a mixture of thallous chloride, sodium carbonate, and potassium cyanide; on leaching the fusion-product with water the thallium remains undissolved.

An electrolytic method has been developed for preparing metallic thallium. The procedure is comparatively simple, since an electrolyte of a thallous compound in aqueous solution is all that is required. The carbonate or sulfate is generally employed, but the best thallium deposits are obtained from a perchlorate bath.[36] It is also possible to obtain metallic thallium by igniting unstable salts or organo-thallium compounds; the element remains behind while the volatile constituents pass off as gases.

In reducing large amounts of thallium it is best to employ metallic zinc. Plates of electrolytically pure zinc, which do not leave a residue when dissolved in sulfuric acid, are arranged vertically about the sides of a deep porcelain dish of from 4 to 5 l capacity. Crystallized thallous sulfate, in amounts of about 7 to 8 lb at a time, is then placed in the dish and enough water is poured over the salt to cover it.

The mixture is then heated so as to insure solution. After prolonged and gentle heating all the thallium salt will be reduced to metallic sponge, which readily separates from the zinc on slight agitation. A process of this kind requires several hours, depending upon the amount of chemicals being treated.

The supernatant liquid containing the zinc sulfate is then poured off and the spongy thallium washed several times. The metal is strongly compressed and preserved under water to prevent oxidation until it is ready to be fused and cast into bars.

Technology

Biological Uses

Thallium is an extremely poisonous substance and finds application as an economic poison. Thallous carbonate, for example, is a very good fungicidal agent, and other compounds, particularly those which are easily soluble, find increasing use for exterminating rodents and other pests. Wheat treated with thallium is a favorite poison bait for killing mice. Unfortunately, however, there have been deaths among children and (less often) among adults due to thallium poisoning. Thallium poisoning is difficult to treat, especially when it has progressed without detection.

In chronic thallium poisoning the hair begins to fall out. This has suggested its use as a depilatory, but such an application is to be greatly discouraged because of the poisonous nature of the substance.

The unusual physiological properties of thallium salts, particularly the sulfate, have been the subject of considerable research by biochemists for many years The acetate has been used in the treatment of ring worm. Doses of 8 mg of the acetate per kilo of bodyweight have been used, but great care is required in handling since doses of half this amount can be toxic under certain conditions. The margin between toxicity and therapeutic benefit is very slim.

The minimum lethal dose for rats and rabbits has been found to be 25 mg per kilogram of body weight. Thallium is cumulative in action. Its most striking effect is to cause atrophy and the loss of function of various endocrine glands. Under controlled conditions thallium salts are useful as rodenticides.[47]

When preparing thallium-poisoned bait for field mice the following formula is suggested by the U. S. Department of Agriculture:

Whole wheat	125	lb
Thallium sulfate	1.5	lb
Hot water	6	qt
Dry starch	0.5	lb
Glycerin	0.5	pt

Thallous acetate has found limited use in medicine for the treatment of certain kinds of tuberculosis and of skin diseases such as ring-worm. There is a possibility that thallous chloride could replace the sulfate in rodent poisons. The chloride, being less soluble, would reduce the danger of accidental poisoning to human beings, because it could be removed from the system before it had an opportunity to be absorbed.

Alloys

Thallium forms alloys with lead, antimony, tin, cadmium, bismuth, indium, silver, platinum and several other metals. Of special interest are the lead-thallium alloys. Contrary to

the usual effect, the addition of lead to thallium, or of thallium to lead, raises the melting point. The alloys formed are highly resistant to ordinary atmospheric and anodic corrosion.[38] The thallium-lead (as well as the thallium-tin and thallium-indium) alloys show super-electrical conductivity at a temperature below that of liquid air.

The amalgam containing 8.5 per cent thallium has a melting point of —60°C (pure mercury melts at —39°C) and can therefore be used for low-temperature thermometers.

An alloy of silver and 16 per cent thallium is highly resistant to hydrochloric acid and hydrogen sulfide.

In the preparation of thallium alloys care should be taken to avoid oxidation or volatilization of the thallium metal. Frequently ordinary melting methods can be dispensed with and more satisfactory results obtained by electro-codeposition from either an aqueous or a fused salt bath, such as a fused borax bath.

None of the thallium alloys may be used in the food industries on account of their very poisonous nature.

Other Uses

Light-sensitive cells are useful where the control of an operation or process can be made to depend on a change in the amount of light transmitted or reflected. The "thallofide" cell is extremely sensitive to wavelengths in the infrared, and has been proposed for signaling in the dark. Thallium oxysulfide is employed in this cell as the photosensitive agent.[39]

One of the standard mixtures used in mineralogy and gemmology for specific gravity determinations is thallium malonate mixed with thallium formate. This is known as Clerici's solution. At room temperature it has a specific gravity of 4.15. Clerici's solution is claimed to be superior to Thoulet's solution in that it is odorless, more mobile, and has only a slight amber color. A similar reageant is Retger's salt, thallium silver nitrate, which is solid at room temperatures, but when heated in a

water bath to 75°C becomes a yellow liquid of density 4.6 g/l. It may be reduced to a lower density by dilution with water.[10]

Thallium salts can be used almost exclusively when high-gravity liquids are required in the gemmological or analytical laboratory. Details of the preparation of these salts are often difficult to obtain. The density of thallium salts employed for specific gravity determinations is easily varied, because they are soluble in water. All of the thallium compounds are, of course, poisonous and should be handled with caution, particularly if the operator has cuts and scratches on his hands.

Thallium formate is used when the specific gravity of the sample lies between 2.95 and 3.5. Slightly higher values may be obtained when the solution is kept on a sand bath. For still higher specific gravities, it is more expedient to use thallium malonate-formate.

In the preparation of thallium formate, pure thallium metal is rolled into thin sheets and cleaned with acetone or ether to remove all grease. The metal, ground to a fine powder or cut into small pieces, is placed on a sand bath and formic acid added to it until the reaction ceases. The solution is poured off and a fresh portion of formic acid added, always maintaining a slight excess of thallium in the reaction vessel. The reaction is accelerated when the thallium is finely ground or when air is bubbled through the solution.

Complete solution of the thallium may take place with some difficulty because of a film of insoluble impurities usually present originally in the metal. Any residue remaining is saved for further processing. The liquid which has been drained off is evaporated to dryness and dissolved in distilled water, re-evaporated, dissolved, and diluted with distilled water to a solution having the desired specific gravity.

To recover the thallium formate after many determinations, the product is washed with hot distilled water, filtered, and then evaporated on a water or sand bath to a high concentration. When washed solutions are allowed to remain on the sand bath,

receiving additions of new washings from time to time, a dark residue may form. This residue consists of oxides and carbonates, which can be dissolved by adding a small amount of concentrated formic acid. The liquid is evaporated to dryness, dissolved in distilled water, and evaporated to expel all free formic acid. Double evaporation assures removal of free acid, which affects sink-and-float determinations. Evaporation should be conducted at temperatures below 130°C, otherwise decomposition may take place.

Solid thallium formate is stored in a dry, dark glass bottle or kept in solution until further use. If the liquid is overheated during preparation, carbon may be precipitated on the addition of formic acid. The carbon may be removed by filtration and the solution reconcentrated as discussed before.

As a liquid of higher specific gravity, thallium malonate-formate is useful, its specific gravities varying between 3.5 and 4.9. This salt may also be diluted with water. It is usually used at temperatures just above 20°C, and is kept on a sand or water bath during the operation.

Thallium malonate-formate is prepared by dissolving 1 mol of thallium formate and 1 mol of thallium malonate in a small amount of water. The thallium malonate is prepared by dissolving thallium metal in sulfuric acid and treating the resulting solution with barium sulfate to precipitate barium sulfate and leave thallium hydroxide in solution. The sulfate is removed by filtration, and the thallium compound in solution is neutralized with malonic acid, and then evaporated to dryness.[41]

Thallium has been introduced at various times as a constituent of special *glasses*, particularly those having unusual optical properties. Thallium is used as a substitute for the lead or other constituents of ordinary glass when a higher refractive index is required.[42]

Thallium salts burn with a bright green flame and, because of this characteristic, are sometimes used for signals and rockets. Flares containing thallium have been employed, but

they are not widely used because of the high cost of the compounds.*

Analysis

Because of its toxicity, it is often important to detect very small amounts of thallium. This is best done spectographically. However, if the analyst does not have a spectograph at his disposal, he may employ the usual wet methods, or the more sensitive, microchemical tests.

In the gravimetric determination of thallium,[44] the element is weighed as the chloroplatinate, the iodide, the chromate, the sulfate, or the acid sulfate. Thomas[45] has developed a method for estimating thallium indirectly from the amount of gold precipitated when auric bromide reacts with thallous chloride.

In the volumetric determination, thallous salts are oxidized with potassium permanganate or treated with potassium iodide.

When thallium salts are introduced into a non-luminous flame they cause a bright and characteristic green coloration. By using a blowpipe on small amounts of concentrates or minerals, thallium may be detected by the color of the flame. A small hand spectroscope may be used to ascertain whether or not the green lines belong to thallium.

Phosphomolybdic acid forms the basis for several chemical tests for thallium. An aqueous solution of this reagent gives a yellowish precipitate with solutions of thallium, cesium and rubidium salts. The test is claimed to be sensitive to 1 part in 500.[46] A thallous salt solution acidified with nitric acid also gives a yellow precipitate with phosphomolybdic acid.[47]

Antimony trioxide may be employed as a reagent for thallium. The antimony compound is dissolved in a slight excess of hydrochloric acid, and water is added until no further precipitation of the oxychloride takes place. The solution is then treated with solid potassium iodide. On addition of this yellow

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* The 1940 quotation for thallium metal was $6.50 per pound.[48]

solution to an acid or neutral solution of a thallium salt, a characteristic orange-to-red precipitate is formed.[48] With sodium ferrocyanide and calcium acetate, thallous salts form a precipitate which is insoluble in water, but soluble in mineral acids. This test is sensitive to 2.5 gammas of thallium per cc of diluent.

Thallium is included along with many other elements in the analytical scheme of Hovorka-Sykora,[49] who use as a reagent a 1 per cent ethanolic isatin-β-oxime solution. Thallium forms a very stable but soluble double salt with this reagent.

Frequently a test for thallic salts must be carried out in the presence of thallous compounds. This is accomplished by a modified Renz procedure. To a dilute solution of thallic salt, made alkaline by potassium hydroxide, there is added a saturated solution of α-naphthol containing a small amount of dimethyl-*o*-phenylene diamine. An indophenol is produced which has a blue color. Even in dilutions of 1 part in 30,000, thallic salts can be detected in thallous compounds. The reaction is determinative only if oxidizing agents, such as ferric ions, are absent.[50]

On adding a saturated aqueous solution of cesium platinous chloride to a solution of thallous chloride a yellow precipitate is formed.[51]

In the test of Picon,[52] a drop of carbon disulfide and an excess of ammonium hydroxide and ammonium sulfide are added to 1 or 2 cc of the solution to be tested. The mixture is heated gently until it begins to boil. The thallium precipitates out as black thallous sulfide, which is transformed into a red complex by carbon disulfide.

The naphthylamines can be used as reagents for thallium. Thallic salts in aqueous solution develop a violet color on precipitation with β-naphthylamine. A silvery crystalline double salt forms.[53]

Another reagent for thallium is mercaptobenzothiazole. In this test, 30 cc of cold solution containing about 0.1 g of a

monovalent thallium salt are treated with an ammoniacal solution of the reagent. The reaction is quantitative, with the formation of a yellow precipitate.[54]

Sodium cobaltinitrite is a very sensitive reagent for detecting thallium in slightly acid solution. It throws down a red crystalline precipitate which is very insoluble in hot water and in cold dilute mineral acids. On boiling with acids, however, the precipitate dissolves with the evolution of nitrogen oxides.[56]

Thallium forms a double salt with uranyl compounds, particularly with uranyl carbonate. This salt crystallizes characteristically and emits fluorescent radiation in the short wavelength visible region. It can be identified under both fluorescence and phosphorescence microscopes. Using the fluorescence microscope, excitation is obtained by 3650Å radiation, whereas with the phosphorescence microscope short-wavelength light, i.e., 2537Å must be used. The test is good for thallous salts only, and thallic ions must be reduced before the test can be applied.

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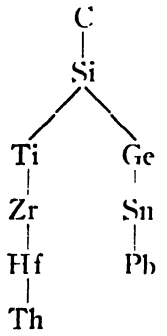
CHAPTER III

GERMANIUM, TITANIUM, ZIRCONIUM, HAFNIUM AND THORIUM

Introduction

The silicon family, consisting of two series of elements, is in the center of the periodic table. Titanium, zirconium, hafnium, and thorium make up one branch of this family, and germanium, tin, and lead, the other. The four elements of the first series are all metallic in nature and have very high boiling points. Their physical properties vary regularly with increasing atomic number. The non-metals, carbon and silicon, are mainly acidic, but the other members gradually become more basic with increasing atomic number. In the other series of the silicon family, we shall be concerned with only one element, germanium, which is comparatively rare. The other representatives of this group are tin and lead.



The relationship of the silicon family of metals to carbon and silicon, and to each other.

It is to be noted that none of the elements of this family is more than superficially oxidized at room temperatures, but all oxidize readily when heated to redness. A common characteristic of all these elements is that they form tetravalent compounds and in some cases also exhibit divalency. Titanium is also trivalent.

Most important in the silicon family is the titanium group, with titanium as its outstanding member. Zirconium and hafnium are less important. Titanium acts like silicon in many circumstances, in fact, some titanium compounds are known to be isomorphous with those of silicon. In a few compounds, titanium resembles silicon and carbon in its ability to form chains.

One of the marked characteristics of the entire group is the tendency to form double salts with halogens. It is also interesting that of the rarer elements in the silicon family all but one consist of five different isotopes, the exception being thorium, which has only one. This can be explained by the fact that thorium is the only one having an odd atomic number.

TABLE 6

PHYSICAL PROPERTIES OF TITANIUM GROUP ELEMENTS

Property	*Titanium*	*Zirconium*	*Hafnium*	*Thorium*
Atomic weight	47.90	91.22	178.6	232.12
Atomic number	22	40	72	90
Atomic volume	10.6	13.97	13.4	20.7
Specific gravity	4.4	6.52	13.3	11.2
Melting point	1850°C	1857°C	2200°C	1845°C
Boiling point	>3000°C	>2900°C	>3200°C	>3000°C
Valences	2, 3, 4	2, 4	2, 4	2, 4
Isotopes	5	5	5	1
Crystal form	hexagonal	hexagonal	hexagonal	cubic

GERMANIUM

History

In 1871 Mendeleeff propounded his periodic table of elements and estimated the atomic weights of elements then not fully investigated. Mendeleeff also predicted the discovery of hitherto unknown elements and corrected the atomic weights of some of the known elements. Germanium was included in the scheme at that time, being indicated as ekasilicon, one of the missing elements. Table 7 compares the predicted and demonstrated properties of ekasilicon.

TABLE 7

PREDICTED AND OBSERVED PROPERTIES OF GERMANIUM

Ekasilicon (predicted, 1871)	*Germanium (discovered, 1886)*
Atomic weight: 72.	Atomic weight: 72.6.
Atomic volume: 13.	Atomic volume: 13.2.
Specific gravity: 5.5.	Specific gravity: 5.47.
Color: Dirty gray, on calcination giving a white powder of EsO_2.	Color: Grayish-white, giving white oxide, GeO_2, on calcination.
Element will decompose steam with difficulty.	Element does not decompose water.
Acids will have slight action.	Element not attacked by HCl.
Alkalies will have no action.	KOH solutions have no action.
Sodium on EsO_2 or EsK_2F_6 will give the element.	Element made by reduction with carbon or sodium.
The oxide will be refractory and its sp. gr. be 4.7; basicity will be less marked than TiO_2 and SnO_2, but greater than SiO_2.	Germanium oxide is refractory, and its sp gr. is 4.703; basicity is very slight.
The chloride will be a liquid boiling under 100°C with a sp. gr. of 1.9.	Germanium chloride boils at 86°C, with a sp. gr. of 1.887.
The fluoride will not be gaseous.	The fluoride is a white solid.
Ekasilicon will form organo-metallic compound Es $(C_2H_5)_4$, boiling at 160°C, with a sp. gr. 0.96.	Germanium forms $Ge(C_2H_5)_4$, boiling at 160°C, with a sp. gr. less than 1.

In 1886, Winkler, a German chemist, analyzed a rare mineral called argyrodite. After eight complete analyses of the mineral he noted that the total was consistently low by about 7 per cent. Accordingly, Winkler came to the conclusion that a new element must be present, and on investigation he suc-

ceeded in isolating the metal germanium and preparing many of its compounds. The typical analysis of argyrodite, Ag_8GeS_6, is:

	Per Cent
Silver	74.72
Germanium	6.93
Sulfur	17.13
Iron and Zinc	0.88
Mercury	0.31

Mineralogy

Germanium is never found in the free state, and the minerals of which it is a major constituent are comparatively scarce. Table 8 gives the most important mineral sources of germanium.

Argyrodite is found in small indistinct crystals, as well as in compact form. It has an uneven flat fracture which may also be conchoidal. It is somewhat brittle, having a hardness of 2.5 and a specific gravity of 6.08 to 6.11. Argyrodite has a metallic luster and a steel-gray color which is most evident on freshly fractured surfaces. It may also have a tinge of red or violet. It was first extensively investigated by Winkler,[1] and was found in the Himmelsfurst mine at Freiberg, Saxony. The mineral is associated with siderite, marcasite, and less often with sphalerite, galena, and other minerals. At Colquechaca, Bolivia, argyrodite is associated with other silver minerals.

TABLE 8

GERMANIUM MINERALS

Mineral	*Composition*	*Per Cent Germanium*
Argyrodite	$4Ag_2S.GeS_2$	6 to 7
Canfieldite	$4Ag_2S.(Ge,Sn)S_2$	1.82
Euxenite	—	Trace
Zinc blendes	—	Trace
Germanite	$7CuS.FeS.GeS_2$	8.7

Euxenite and some zinc blendes carry varying amounts of germanium. In a spectographic study, Papish [2] found that all specimens of cassiterite, and thirty-four specimens of topaz from twenty-seven localities, contained the metal.

Germanite is an important germanium mineral, containing also about 44 per cent arsenic, 2.7 per cent zinc, 5.6 per cent iron, and from 1 to 2 per cent lead. At present this mineral comprises one of the main sources of the element.[3]

By spectroscopic technique the presence of germanium has been established in mineral waters of Gerez in Portugal.[4] The germanium content proved that the water had its origin in primitive rocks. The same method has also demonstrated the presence of germanium in stannite, native copper, pyrargyrite, and calamine. A specimen of pyrargyrite (Ag_3SbS_3) from the silver mines of Bolivia showed over 1 per cent germanium.[5]

Physical Properties

Germanium metal is a gray-white crystalline solid, which retains its fine luster in air. It is a very brittle substance, crystallizing in regular cubes. Germanium begins to volatalize at its boiling point, about 2700°C. It consists of eight isotopic species.[6] The physical data for germanium are given in table 9.

TABLE 9

PHYSICAL PROPERTIES OF GERMANIUM

Property	*Value*
Atomic weight	72.60
Atomic number	32
Atomic volume	13.2
Isotopes	70, 71, 72, 73, 74, 75, 76, 77
Specific gravity	5.36
Melting point	958.5°C
Boiling point	2700°C(?)
Specific heat at 0° to 100°C	0.074 cal.
Resistivity	0.0735 ohm-centimeter
Usual color	Grayish-white

Electrical Properties

Bidwell [7] prepared a rod ($2.4 \times 0.44 \times 0.41$ cm) of very pure germanium and investigated the change in its electrical conductivity with temperature. Upon plotting the resistance against the temperature, a very interesting curve was obtained. Starting at liquid air temperature the electrical resistance decreases, reaches a minimum at about —776°C, then increases, and reaches a maximum at about 165°C. This curve is entirely different from most resistance-temperature curves for metals. As a general rule, they show an increase in resistance with temperature. The curves for other metals of the carbon group, notably those for zirconium, silicon, titanium, and tin, are similar to that for germanium.

It seems to the writers that a practical application of this electrical property of germanium will appear as soon as the metal can be prepared at a much lower cost than is possible at present. A simple temperature-regulating device for maintaining an oven or a radiator at 165°C would not be difficult to devise from germanium.

Chemical Properties

Germanium metal is stable in the air. It burns when heated in a flame, giving off white vapors, which condense on cooling to the dioxide, GeO_2. Metallic germanium is insoluble in hydrochloric acid and resists the action of many other acids, and the alkalis. However, nitric acid and aqua regia dissolve it. Hydrogen peroxide is another good solvent.

Germanium exhibits metalloid rather than metallic properties. The nitrate is unknown, but two nitrides (Ge_3N_2 and Ge_3N_4) have been isolated. The sulfate is difficult to prepare and hydrolyzes readily.

Heating finely divided germanium metal to 900°C in oxygen converts it readily to GeO_2. Heating it at relatively low temperatures in bromine vapor causes it to ignite, producing $GeBr_4$. In sulfur fumes (at 250°C) GeS_2 is formed, and in

SO_2, both the sulfide and the oxide are formed. (A platinum crucible is not to be used for these experiments, since germanium readily combines with platinum to form a brittle, low-fusing alloy).

Germanium is the only element (besides carbon) of the fourth group of the periodic table which forms a dioxide that is appreciably soluble in cold water.

Compounds

Black, crystalline germanium monoxide, GeO, is readily prepared. It is fairly stable in air and distinctly basic in nature. It reacts with the halogen acids forming dihalides, and reduces hydrogen peroxide and potassium permanganate. It is less stable than the monoxides of tin and lead.

Upon burning germanium metal in oxygen, the white, crystalline dioxide, GeO_2, is formed. It is readily soluble in alkalis but relatively resistant to acids.

Germanium dihalides are not difficult to prepare. They are less stable than those of tin and lead. These compounds unite with free halogens to form tetrahalides, just as do the corresponding tin compounds. In addition, germanium resembles carbon and silicon in that it forms compounds similar to chloroform with gaseous halogen acids.

Germanium forms a monosulfide which is stable. In this respect it resembles lead and tin, but not carbon and silicon. Germanium disulfide is precipitated by hydrogen sulfide. Since it is quite soluble in water, it should be prepared in a high acid concentration for complete precipitation. The sulfides are important because they are involved in the production of the metal.

The dioxide is prepared from sodium sulfogermanate, which can be obtained by fusing germaniferous minerals with sulfur and sodium carbonate, and extracting the sodium salt with water. The solution obtained is then treated with hydrochloric acid, and germanium disulfide separates out as a white, voluminous precipitate which is soluble in water but insoluble in acids.

The sulfide can either be ignited or treated with nitric acid to obtain the monoxide, which is reduced to the metallic state by hydrogen or powdered charcoal.

Germanium dioxide in the hydrated form is prepared by the action of water on the tetrachloride. The product resembles hydrated silicon dioxide in that it is somewhat soluble in water. Germanium dioxide, like silicon dioxide, melts at high temperature to a clear glass-like mass, which may be substituted for silica in some glass mixtures. On the other hand, quite a difference is noted between germanium dioxide and the corresponding tin and silicon compounds. The germanium compound, when heated with concentrated hydrochloric acid, quickly and completely forms a volatile tetrachloride.

The tetrahalides of germanium are rather stable. The tetrachloride does not dissociate at 950°C, but the tetraiodide dissociates into the diiodide and free iodine at 440°C. Germanium tetrachloride also shows stability toward various reducing agents and easily reduces tetravalent tin to the divalent state.

There are a number of analogies between germanium and carbon and silicon. These are exemplified by the formation of hydrides and organic compounds. The following germanium hydrides have been prepared and studied:

GeH ..... germanium monohydride
GeH_4 ..... monogermane tetrahydride
Ge_2H_6 ..... digermane hexahydride
Ge_3H_8 ..... trigermane octahydride

Numerous organo-germanium compounds have been prepared.[9] A very good listing of 116 compounds of this nature is to be found in the work of Hodgman and Holmes.[10]

When germanic salts are treated with zinc and 25 per cent sulfuric acid, a voluminous, flocculent precipitate of stable, dark-brown germanous oxide is formed. This reaction may be

used as a test for germanium, enabling the detection of 100 gammas of the element. Germanic salts may also be reduced at 100°C by hypophosphorous acid. Germanous solutions give an orange-brown hydroxide with ammonium hydroxide, a red sulfide with hydrogen sulfide. Germanous chloride reduces gold and silver salts and potassium permanganate.

Extraction from Ores

Germanium may be extracted from its ores by wet methods, or by fusion and subsequent elution with water or acid solution. Zinc blende, for example, is treated with sulfuric acid and evaporated to dryness. The residue is dissolved in water and sodium sulfide added to precipitate the sulfide of germanium, which is then treated with a 15:100 sulfuric acid solution. Zinc sulfide dissolves, leaving germanium sulfide alone in the solid phase.

As pointed out by Browning, germanium can be separated from most elements by using ammonium sulfide to form the soluble sulfogermanate, and then acidifying the solution to precipitate the sulfide. Separation of germanium from arsenic, tin, and antimony is accomplished by neutralizing the sulfo-salt solution with sulfuric acid, allowing to stand 12 hours, and filtering. The filtrate is evaporated to a small volume, treated with ammonium hydroxide and ammonium sulfate, acidified with sulfuric acid, and saturated with hydrogen sulfide. Germanium sulfide is precipitated.

One of the latest schemes applied to the extraction of germanium is that of Tchakirian.[11] This method will be discussed rather fully, because it is based on the use of oxalic acid, the "queen" of the acids in rare-metals treatment. Time and again when the strong mineral acids fail to attack rare metal ores, oxalic acid is comparatively effective.

Tchakirian applied his extraction method to Southwest African ore carrying germanium, sulfur and copper. Assays revealed 4 to 5 per cent Ge. Other metals present included Fe, As, Zn, Mo, Pb, W, Ti, Ni, Co, Cd, Ag, V, Bi, Se, Te, In

and Ga (0.25 per cent). Treatment is based on the fact that GeO_2 is only slightly soluble in H_2SO_4 and HNO_3 but very soluble in the bioxalate of ammonium. Solutions of the germanium oxalate are not decomposed by H_2S, thus permitting the elimination of the other metals by precipitating with H_2S.

The germanium ore is pulverized and treated with concentrated HNO_3. The insoluble residue, containing the Ge and a little Pb, As, W, Mo and Fe, is treated with a hot solution of oxalic acid and ammonium oxalate and boiled for 24 hours. The germanium goes into solution almost 100 per cent as germanium acid oxalate.

This acid solution is next treated with H_2S and the insoluble sulfides filtered off. To the filtrate $(NH_4)_2S$ is added, the germanium remaining in solution as a complex salt. The solution is heated with H_2SO_4 and a little HNO_3 until white SO_3 fumes appear. The germanium is thrown out as spectroscopically pure GeO_2.

Preparation of the Metal

Metallic germanium may be obtained by reducing germanium dioxide with carbon under a flux of sodium chloride. A yield of about 90 per cent is obtained, and the technique is claimed to be quick and applicable to any amount of material.[12] Germanium does not form a carbide.

The metal can be electrodeposited from alkali oxalate, tartrate and phosphate solutions, but so far, only very thin deposits have been possible.[13]

Finally, germanium dioxide can be reduced to the metal with hydrogen at 540°C.[11]

Technology

The practical applications of germanium are few. The metal forms alloys having excellent physical and chemical properties, but the demand has not yet become great enough to warrant large-scale production.

A germanium-silver alloy containing 74 per cent silver and

the remainder germanium is a eutectic. Alloys of germanium with light metals have been prepared and studied by the United States Bureau of Standards,[15] but their importance has not yet been proved.

Kroll [16] has developed alloys of germanium, aluminum and magnesium. He prepared eleven different alloys of this nature. One series consists of germanium and aluminum, containing from 0.92 to 60 per cent germanium, 0.25 per cent silicon, and 0.45 per cent iron. Another series contains 40 per cent germanium in combination with varying quantities of the other metals. The alloy of 40 per cent germanium with magnesium is harder than silicon, having a hardness of 82 Brinell.

The copper-germanium eutectic is formed at 35 per cent germanium. Up to 17 per cent, the alloys are a golden yellow, but Cu_3Ge is silver-white with a bluish cast. Alloys having more than 25 per cent germanium are attacked by aqua regia only; concentrated sulfuric acid has practically no effect. The hardness and brittleness of copper is increased considerably by the addition of germanium (cf. copper-silicon alloys).

Analysis

Comparatively few methods have been developed for the precision assay of germanium. The earliest tests were those which depended upon precipitation of the element as the sulfide from acid solutions of germanous salts. The procedure is to saturate the solution, acidified with hydrochloric acid, with hydrogen sulfide. The germanic and germanous sulphides are precipitated as a white voluminous mass which is dried, ignited, and weighed as the germanous oxide. Germanic sulfide is insoluble in acids but dissolves readily in water; it can be reprecipitated by the addition of acids, particularly when hydrogen sulfide is introduced.

The method of Browning,[17] discussed previously, may also be employed for the detection of germanium.

For detecting small amounts of germanium in the absence of

silica and phosphates, a slightly acid test solution is placed on filter paper, and 1 drop of a solution of 1.5 g of ammonium molybdate in 10 cc of water and an equal amount of concentrated nitric acid are added. A drop of 0.1 per cent solution of benzidine in acetic acid and sodium acetate solution are added, or, the paper is held over the mouth of a small bottle containing ammonium hydroxide. A positive reaction for germanium is indicated by the formation of a blue color.[19]

Poluetkov [21] has given a test for germanium in which a 0.01 per cent solution of hydroxynaphthalenequinone sulfonic acid in concentrated sulfuric acid is added to the solution to be tested. A bright pink color observed in blue light indicates germanium. It is the opinion of the writers that examination in ultraviolet light constitutes a more effective procedure, based on fluorochemical principles.

The precipitation of white germanium sulfide from alkaline solutions comprises a fairly delicate test for the element. The test solution is made alkaline, and first ammonium sulfide, then hydrochloric acid is added. To detect germanium in the presence of arsenic, a mirror is made by electrolytic reduction with sodium amalgam, or reduction with aluminum and potassium hydroxide. The arsenic must be present as the arsenate.

One method for the volumetric determination of germanium depends on the fact that 10 g of germanic oxide will dissolve in 1 l of water containing 20 g of mannitol.[18] The solution reacts as a monobasic acid, and it can be titrated with sodium hydroxide, using phenophthalein as the indicator. If 20 g of calcium chloride are added to 10 cc of the germanium solution, it reacts as a dibasic acid.

When an aqueous solution of germanic oxide is treated with a mixture of potassium iodide and potassium iodate, at the end of 3 hours, 1 gram-atom of iodine is formed for each gram-atom of germanium. In the presence of strong electrolytes, 1 gram-atom of iodine per gram-atom of germanium is liberated in 12 hours.

Strong acid is eliminated by the iodide-iodate mixture and the solution carefully decolorized with sodium thiosulfate. Mannitol is added, and the solution allowed to stand for three hours. The germanium is titrated directly with the thiosulfate.

The use of organic reagents for germanium analysis has been described by White.[19] It is pointed out that germanic acid reacts with many reagents in the same way as boron. For example, cochineal tincture gives orange-yellow fluorescence with boric acid, with germanium salts, and with molybdates.[20] Quinalizarin is also recommended as a reagent for germanium.[21]

For the detection of minute quantities of germanium, the spark spectrum may be examined for characteristic blue and violet lines. The blue line at 4686Å is particularly distinctive.

Titanium

History

The discovery of titanium is due to Gregor,[22] an English priest, who in 1791 first found the new substance in a magnetic sand from Menachan Parish Cornwall. The magnetic sand, named *Meanchanite* after the parish, led Gregor to call the new element *menachin*. Four years later, Klaproth, while analyzing the mineral rutile, found a new element which he called *titanium*. Subsequently it was shown that both substances were identical, but the name introduced by Klaproth was permanently accepted.

Crude titanium metal was first isolated in 1825 by Berzelius. Later, Rose and Wöhler prepared and studied the new element, contributing much information about its chemical properties. They also prepared numerous compounds of titanium. In 1910, Hunter [23] prepared Ti metal of 99.9 per cent purity by reducing $TiCl_4$ with metallic sodium.

Rossi, in 1895, produced ferrotitanium. Commercial production of ferrotitanium in the electric furnace was introduced at Niagara Falls in 1906.

Mineralogy

Contrary to popular opinion, titanium is a relatively common element in the earth's crust. According to Clarke and Washington,[24] the average percentage of titanium in igneous rocks is 0.63, making it eighth in abundance. It is outranked only by silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. However, titanium can be considered in the class of "rarer metals" because its uses and technology are not very well known.

Titanium is never found in the native state, but several of its important minerals are practically pure titanium dioxide. It is present in numerous minerals and, in fact, it becomes a complicating factor in the processing and recovery of many other metals from their ores, particularly the rarer metals. In chemical analysis, titanium is frequently encountered, especially in spectrochemical investigations of minerals and alloys.

TABLE 10

TITANIUM MINERALS

Mineral	*Composition*	*Per Cent Titanium Oxide, TiO_2* ‡
Astrophyllite	$(Na,K)_4(Fe,Mn)_4Ti(SiO_4)_4$	7–14
Benitoite	$BaTiSi_3O_9$	20
Blomstrandite	Complex	10–19
Brookite	TiO_2	90–100
Derbylite	$6FeO.5TiO_2.Sb_2O_5$	34–35
Delorenzite	Complex	66
Dysanalyte	$6(Ca,Fe)Ti(O_3.(Ca,Fe)Cb_2O_6$	40–59
Eschynite	$R^{III}_2Cb_4O_{13}.R^{III}_2(Ti,Th)_3O_{11}$	21–22
Euxenite	$R^{III}(CbO_4)_3.R^{III}_2(TiO_4)_2.3\frac{1}{2}H_2O$	20–23
Geikielite	$MgO.TiO_2$	67–68
Guarinite	$CaTiSiO_5$	33–34
Ilmenite *	$FeTiO_3$	3–59
Knopite	$RO.TiO_2$	54–59
Leucosphenite	$Na_4Ba(TiO)_2(Si_2O_5)_5$	13–14
Lewisite	$5CaO.2TiO_2.3Sb_2O_5$	11–12
Lorenzite	$Na_2(TiO)_2Si_2O_7$	35

Mineral	*Composition*	*Per Cent Titanium Oxide, TiO_2* ‡
Narsarsukite	Complex silicate	14
Neptunite	$\overset{I}{R_2}\overset{II}{R}TiSi_4O_{12}$	17–18
Octahedrite	TiO_2	90–100
Perofskite	$CaTiO_3$	58–59
Polycrase	$\overset{III}{R}(CbO_3)_3.2\overset{III}{R}(TiO_3)_3.3H_2O$	25–29
Polymignite	$5RTiO_3.5RZr_3.R(Cb,Ta)_2O_6$	18–19
Pseudobrookite	$Fe_4(TiO_4)_3$	44–53
Pyrochlore	$RCb_2O_6.R(Ti,Th)O_3$	5–14
Rutile *	TiO_2	90–100
Schlormenite	$3CaO(Fe,Ti)_2O_3.3(Si,Ti)O_2$	12–22
Senaite	$(Fe,Pb)O.2(Ti,Mn)O_2$	57–58
Titanite (Sphene)	$CaTiSiO_5$	34–42
Tscheffkinite	Complex silicate	16–21
Yttrocrasite	Complex titanite	49–50
Zirkelite	$(Ca,Fe)O.2(Zr,Ti,Th)O_2$	14–15

* Ilmenite and rutile are commercially the most important minerals.
‡ TiO_2 contains 59.95 per cent Ti.

Rutile and Ilmenite

The two commercial minerals that serve as raw material for over 90 per cent of the titanium alloys and compounds produced are rutile and ilmenite, TiO_2 and $FeO.TiO_2$ respectively. Commercial rutile carries up to 60 per cent titanium and is the purer and more desirable of the two minerals. However, ilmenite, containing about 32 per cent titanium, is cheaper and much more plentiful than rutile. For the production of ferrotitanium and the white pigment, TiO_2, ilmenite is usually preferred.

Rutile crystallizes in the tetragonal system, commonly as short, stout, translucent prisms, or elongated prisms frequently showing striated prism faces. Rutile is very resistant to acids but dissolves in alkalis. The color of the rutile crystals varies from brown to red, yellow, blue, violet, green and black.

The formula of ilmenite is frequently given as $FeTiO_3$. It crystallizes in the hexagonal system. Ferric oxide, Fe_2O_3, and

titanium oxide, TiO_2, unite in all proportions to form a series of compounds varying in composition between the limits, TiO_2 (rutile) and Fe_2O_3. Ordinary ilmenite contains about 32 per cent titanium and 37 per cent iron. Its hardness is between 5 and 6. Ilmenite furnishes about 96 per cent of the world's titanium. It is important as the raw material for making the white pigment, TiO_2.

An important commercial rutile locality is Nelson County, Virginia. For years this country has been exporting substantial quantities of rutile. In Europe there are extensive rutile deposits at Kragero, Norway. Other important localities of ilmenite ore are the Adirondacks, Essex County, New York,[25] and Travancore, British India.

Physical Properties

Metallic titanium, as prepared by Hunter,[26] has a bright silvery luster, and when polished resembles steel in appearance. It is rather brittle at ordinary temperatures, although this property depends somewhat upon its mode of preparation and grain size. At low red heat titanium is readily malleable. Titanium melts at about 1850°C and boils at a temperature above 3000°C. Titanium is a light metal, having a specific gravity of 4.4.

In the preparation of pure titanium, recent advances can be credited to Kroll of Albany, Oregon.[27] The titanium prepared by the Kroll process has a hardness of 180 to 200 Brinell at room temperature and 87 Brinell at 400°C. The purity is in excess of 99.8 per cent.

Buttons and granules of very pure titanium, obtained by a process described in the following section, are not as malleable as sintered titanium, which is somewhat malleable in the cold. Colloidal titanium having pyrophoric properties may also be prepared for use in photo-flash bulbs.

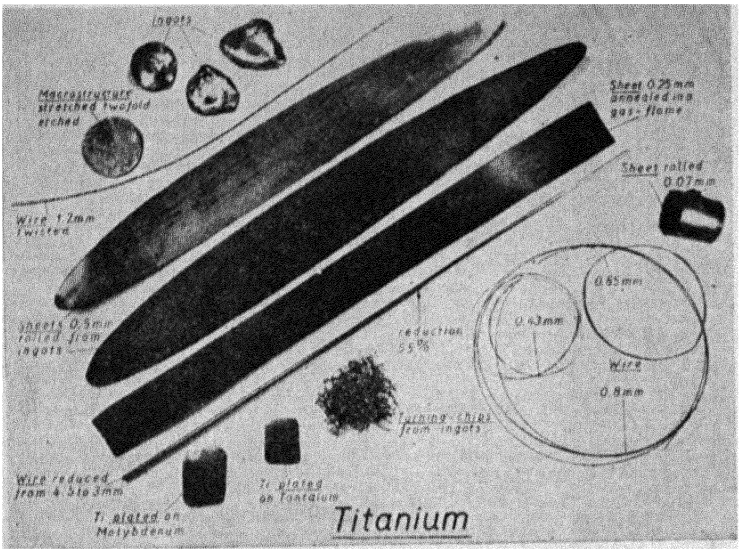


FIGURE 3

Products made of titanium metal and titanium-clad tantalum and molybdenum [Kroll, *Trans. Electrochem. Soc.*, **78**, 45 (1940)].

Kroll's pure titanium, in the form of wire, rod, and sheet, may be bent when cold to an angle of 180°, if the material is less than 1 mm thick. Heating to above 800°C embrittles the metal and increases its grain size. Titanium is easily rolled, and in wire form can be swaged like tungsten at 500°C, with a 25 per cent reduction in diameter. A 10 per cent reduction is possible by drawing while hot through tungsten carbide dies heated dark red. In drawing, it is essential that an oxide film covers the surface of the titanium wire to provide lubrication and prevent the wire from sticking to the die. The oxide film is produced by heating in a gas flame.

Chemical Properties

Pure titanium is an extremely active metal, and therefore, precautions must be taken to exclude oxygen and nitrogen during its preparation. Like other metals of the same group, e.g., zirconium and hafnium, and like the elements of the fifth group, vanadium, columbium and tantalum, titanium is a gas-sensitive metal. It readily takes up both nitrogen and oxygen, which cannot be expelled by vacuum treatment. When both of these gases are present in titanium the physical qualities are markedly changed and the metal becomes cold-brittle. Hydrogen is absorbed by titanium with the formation of an indefinite compound, made up of 1 part titanium and 1.73 parts hydrogen, possibly a hydride, which decomposes upon heating in a vacuum to 1000°C.

Metallic titanium does not decompose water at ordinary temperatures, although it has a slight effect on heated water. It is readily attacked by warm hydrochloric acid. Dilute hydrofluoric, nitric, sulfuric, and acetic acids dissolve it. Titanium combines with the halogens, especially chlorine, and forms the nitride with nitrogen. When heated in air or oxygen it burns very vividly with the emission of light resembling an electrical discharge.

Compounds

Titanium exhibits three valences: two, three, and four. It forms the three oxides and hydroxides corresponding to each of these valences, the most common oxide being the dioxide, TiO_2. The bi- and trivalent derivatives of this element are powerful reducing agents. Many of the titanium compounds closely resemble tantalum and columbium compounds in their behavior toward chemical reagents. Nearly all titanium salts are insoluble in water. To dissolve these salts, fusion or treatment with free acid is necessary.

Titanium dioxide is the outstanding titanium compound; the major consumption of titanium is as the dioxide. There are

three crystallographic modifications known. When the compound is precipitated by the usual process, it is obtained as an apparently amorphous product, as are all hydrated oxides of the same metal series.

For technical use as a pigment, however, the dioxide must be in cryptocrystalline form, and the change from the amorphous to the crystalline form must be brought about either by heating or by means of special precipitating processes. Pure, crystallized titanium dioxide has the highest refractive index (2.55) of all known white substances. It melts at 1560°C and withstands the influence of light. It has the low specific gravity of 3.8. Titanium dioxide is chemically inert and is not affected appreciably by water, organic solvents, dilute acids, alkalis, hydrogen sulfide, sulfuric acid, carbonic acid, or ammonia.

Titanium combines with chlorine to form the tetrachloride (melting point, —30°C), which is a colorless liquid that fumes in air. Volatile titanium compounds are important constituents of a number of war gases. Titanium combines with strong acids, although it does not react with the weak acids. With fused alkalis, titanium dioxide unites to form titanates. The dioxide is less basic than zirconium oxide. Titanic acid, $Ti(OH)_4$, is precipitated from its salts by alkalis. It resembles silicic acid in many of its properties. Titanium compounds show some similarity to those of silicon, a fact which may be explained by the proximity of the two elements in the periodic table.

Titanium is one of the few elements which burn vigorously in nitrogen (800°C).

Extraction from Ores

There are many methods of extracting titanium from its ores. The important alloy ferrotitanium, used in metallurgy, can be prepared directly by adding rutile to a molten mass of iron and aluminum, or ferrosilicon.

The finely pulverized titanium mineral may be fused with 6 parts potassium bisulfate and extracted with water, and

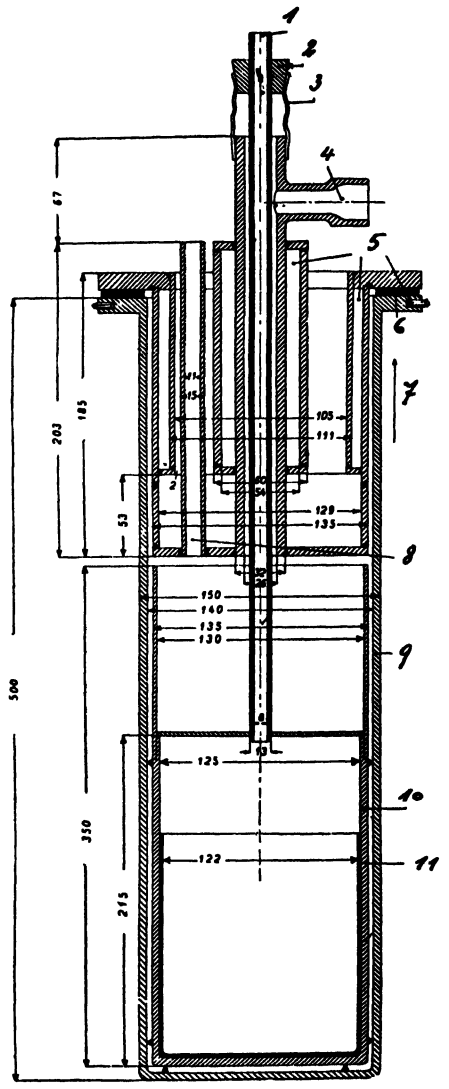


FIGURE 4

Kroll's titanium reduction furnace.

1 inlet for titanium tetrachloride; 2 rubber plug; 3 rubber tire; 4 vacuum pump connection; 5 water-cooling; 6 rubber gasket; 7 lead coil cooling means; 8 opening for getter electrode; 9 nichrome container; 10 iron crucible; 11 molybdenum lining [Kroll, *Trans. Electrochem. Soc.*, **78**, 43 (1940)].

ammonium sulfide added to the solution to precipitate titanium hydroxide. The ferrous sulfide, which is also precipitated must be separated from the hydroxide. Titanium ore may be fused with sodium peroxide and the fusion-product extracted with water, the titanium remaining in solution.

When titanium ore is fused with potassium acid fluoride, the titanium enters into combination as potassium fluotitanate, a compound which is soluble in water slightly acidified with hydrofluoric acid.

Titaniferous magnetite can be treated with 20 per cent hydrochloric acid at 100°C to remove about 98 per cent of the iron. When the residue is chlorinated at 400 to 500°C, gaseous $TiCl_4$ is evolved.

Preparation of Ferrotitanium

Wartman[25] has described at least three processes for the production of commercial ferrotitanium. One is a modification of the thermit process. The thermit process itself cannot be used to obtain titanium in the pure state, because the heat of reaction is not great enough. However, it can be employed to reduce a mixture of 1 part titanium oxide with several parts iron oxide to give ferrotitanium which may contain from 22 to 42 per cent titanium, 3 to 8 per cent aluminum, and very little carbon.

Technology

Pure titanium metal finds little use as compared to its ferroalloy and various compounds, especially the oxide. Ferrotitanium in small amounts is added to molten steels for refining purposes. Titanium renders steel ferritic; any titanium nitride formed passes into the slag. An important use of ferrotitanium is in high-chromium steels. Titanium causes grain refinement and eliminates ingotism when present in amounts greater than 1.11 per cent. The titanium combines with the carbon in the

steel. The TiC is soluble at 1400°C and therefore subject to rearrangement by heat treatment.[29] Titanium has a greater affinity for carbon than has chromium.

The introduction of a small percentage of titanium, about 0.2 per cent, increases the tensile strength of both coke and charcoal iron. To introduce titanium into these irons, use is made of a ferrotitanium alloy containing from 10 to 12 per cent titanium, which is added to the furnace. For the cupola, the best results are obtained by adding the alloy in small, crushed pieces. Ferrotitanium has been manufactured free from carbon, containing either 20 to 25 per cent or 45 to 55 per cent titanium.

The Grainal alloys, mentioned in the section on vanadium, find wide use as deoxidizers, supplanting manganese under certain conditions. The complex Grainal alloys are made up of aluminum, titanium, and a hardening agent such as vanadium. Titanium intensifies the hardening effect of the vanadium so that less of this more expensive metal is needed. The aluminum and titanium develop fine-grained metal by deoxidation, giving the metal a desirable combination of strength and ductility, which persist when it is quenched and drawn. This treatment is applied chiefly to forging steels containing about 0.4 per cent carbon and 1.8 per cent manganese.

The amount of pure or alloyed titanium represents, at present, only a few per cent of the total amount consumed. Most of the titanium used in the metallic state is in the form of alloys such as ferrotitanium, ferrocarbontitanium, cuprotitanium, etc. These alloys are added to molten metal as scavangers just before casting. Ferrocarbontitanium is the cheapest of these alloys and is the one most employed as a deoxidizer in steel and gray cast iron. It is added in amounts up to a few pounds per ton just before casting. For carbon control purposes, the more expensive ferrotitanium is employed.

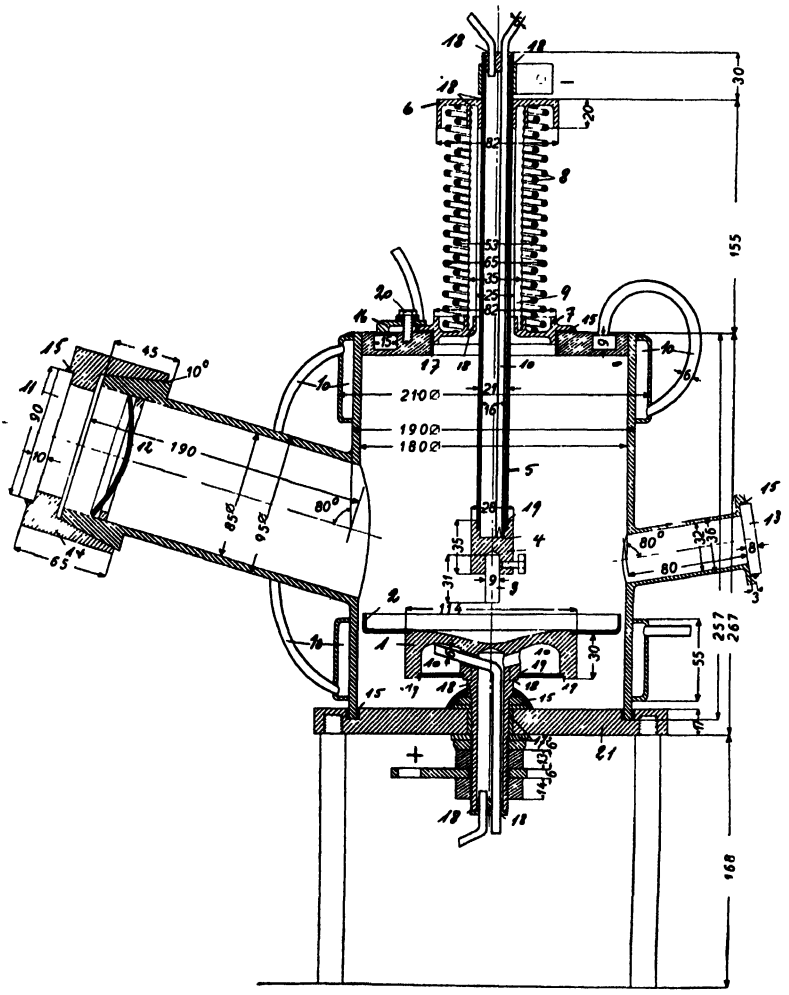


FIGURE 5

Titanium vacuum arc furnace [Kroll, *Trans. Electrochem. Soc.*, 78, 43 (1940)].

1 water-cooled copper anode; 2 iron cup; 3 tungsten rod; 4 water-cooled copper block; 5 water-cooled tube; 6 brass cap; 7 brass collar; 8 springs; 9 flexible red brass tube, 10 water cooling; 11 quartz window; 12 watch glass; 13 quartz window, 14 conical cap; 15 picein rubber cement; 16 clamps for cathode holder; 17 mica gasket; 18 soft solder; 19 hard solder; 20 flexible cathode holder; 21 metal base (dimensions are in millimeters).

The titanium in iron increases its transverse strength and gives greater density to the metal. It imparts a harder chill or wearing quality to a wheel made from such iron. Therefore, in the manufacture of car wheels, axles, and rollers, titanium-reinforced steel is very useful. The use of titanium carbide in sintered hard alloys for machine tools is a recent development.

High-melting alloys containing titanium have been developed. One such alloy is composed of 20 per cent molybdenum, 5 to 80 per cent tungsten, and 0.5 to 4 per cent carbon. The tungsten may be replaced with tantalum, and the molybdenum with titanium. Titanium, when added to chrome steel, greatly reduces brittleness. Titanium is also added to steel along with zirconium. Titanium can be added to ferrous alloys to increase cementation.

Certain titanium alloys may be employed as filaments in vacuum tubes. The importance of such an alloy is that it replaces the more expensive iridium-platinum alloy. The titanium alloy consists of ferrotitanium, cobalt, and nickel. It gains tensile strength as it grows hotter, but it oxidizes slightly at elevated temperatures and its efficiency is thus reduced.

Wartman [25] has pointed out that titanium carbide is harder than tungsten carbide, although it is not as good a conductor of heat. For this reason, the use of titanium carbide on the tool edge is desirable if maximal hardness is essential, otherwise it is detrimental, since the lower heat conductivity adversely affects the life of the tool.

Little use has been made of titanium in precious-metals metallurgy, but such applications may soon appear. Alloys of titanium with platinum metals, silver, and gold should have very interesting properties. For bearings and specialized uses, such as in facing surfaces which must resist corrosion and possess other unusual physical properties, the alloys of titanium with tantalum and columbium may also be of interest.

Titanium forms alloys with many other metals, including

the very soft metals, such as thorium. Columbium hardens titanium, although as much as 20 per cent columbium does not impair the hot-rolling properties of the alloy. It is possible to prepare titanium alloys containing up to 40 per cent tantalum which have interesting properties. Of the many elements which have been studied in combination with titanium, only a few, such as silicon, tend to render it brittle; usually, malleability and ductility are the result.

It is comparatively easy to clad molybdenum, tungsten, and tantalum with titanium. This has been done by fusing titanium with a high frequency current onto a sheet of the other metal. The titanium-clad metal is then rolled hot into the desired form. Molybdenum and tungsten harden titanium appreciably, although tantalum does not harden it to any extent. The alloy-layer bond between the clad metals is soft enough to permit bending in the cold without breaking.

Uses of Titanium Dioxide

The most important compound of titanium is the dioxide, TiO_2. Most of the titanium dioxide is obtained from ilmenite, and to a lesser extent from other titanium ores. It owes its popularity to the excellent properties which render it useful as a white pigment. It is used extensively as a pigment in paints with oil or other binding substances, and it has also been used by many trades to impart a white or other light color to many products, such as linoleum, oilcloth, artificial leather, rubber goods, synthetic resins, celluloid and other plastics, paper, cloth, etc. It is also possible to give lighter shades to badly colored masses, allowing them to be dyed in clear and lustrous colors afterwards.[40]

It has been shown by both laboratory and field tests that titanium dioxide is in many respects greatly superior to white lead or zinc white as a pigment. Titanium dioxide is characterized by a high obscuring power, greater covering capacity, fastness to light and heat, excellent elasticity, and resistance

to acid fumes. Moreover, titanium dioxide lacks the poisonous properties of the lead and zinc oxides.

Titanium dioxide, being resistant to salt air and water, is excellent for enamels. It should be ground into a stiff paste with about 23 per cent linseed oil before being incorporated into the paint. It may also be blended with precipitated barium sulfate, zinc oxide and lead oxide. The titanium paste is thinned with linseed oil and various dryers for use as a paint.

The high opacity of titanium dioxide pigments is utilized not only in paints and decorative coatings, but also in cosmetics, rayon and food products. In paper making, the pigments can be introduced in a medium of glue, casein, and starch. Their ready retention by paper pulps makes them useful as beater fillers for improving the opacity, color, brightness, etc., without increasing the loading of the paper. For compounding white and colored rubber, the dioxide and calcium-base pigments are used because of their fine particle size, high opacity, and chemical inertness.

Titanium-barium pigments are employed for similar reasons in leather manufacture, to drum wet skins for making white or light-colored leathers. By dispersing some of the titanium pigment into a viscose solution before spinning, the luster of the rayon is controlled without clogging spinnerets or weakening the material. As it causes no irritation and is non-poisonous, titanium dioxide finds increasing use in the cosmetic field, as a whitener in face powders, skin lotions, cold creams, etc. Additions of 1 per cent of the oxide greatly improve the appearance of white soap.

The addition of titanium dioxide to rubber causes softening, a factor of importance during milling. Its softening property also limits its use as an accelerator for obtaining a strictly white vulcanite, when it is used as the only white pigment. When added to linoleum, the oxide is an ideal pigment, because it is non-poisonous, has low specific gravity, and great tinting strength. Other oxides have various disadvantages: the oxides

of zinc, magnesium, and calcium result in hardening with fatty acids, white lead is poisonous, and lithopone (containing sulfur) may cause darkening.

In ceramics, titanium dioxide is an important opacifying and coloring agent. When titanium is added to clay ware, and the ware is burned to the sintering point, or if a reducing fire is employed, a purplish color develops.

The oxides of titanium, barium, and uranium have been employed in raw yellow glazes. The action of titanium dioxide upon glazes is often similar to that of calcium oxide and zinc oxide. Titanium phosphate has been used instead of the oxide as a pigment and in glass.

Uses of Other Titanium Compounds

Titanium ferrocyanide has found some application in the arts because of its fine green color. It is prepared by adding potassium ferrocyanide to a solution of hydrated titanic oxide in hydrochloric acid, then washing and drying the green powder. It can be used as a substitute for the poisonous Schweinfurth green and other arsenical pigments.

Rutile or titaniferous magnetite, titanium carbide, and titanium dioxide have all found limited use as electrodes in electric arc lamps. Electrodes made of titanium carbide give better efficiency, superior color and light, and cost less to maintain. Titanium in welding rods holds the arc more firmly than any other substance.

Some titanium compounds, such as the dioxide, find use in porcelain tile, and artifical teeth for imparting a yellow color or an impervious glaze to the surface. A few titanium compounds may be employed in pyrotechnics because of the bright light they emit during combustion. Soluble titanium salts, such as the chloride and the sulfate, are used in the dyestuff industries for mordanting. Volatile titanium halides find application in warfare for smoke cloud and dense fog formation.

A titanium cathode is used in a special photoelectric cell

having maximum sensitivity at 2800Å. The cell is used in determining the erythemogenic values of various sources of radiation.[31]

Analysis

Titanium is usually determined as the dioxide, obtained by precipitating with ammonium hydroxide or by boiling a titanium solution acidified with acetic or sulfuric acid. Several methods for the volumetric determination of titanium are also known. They depend upon color formation, or the reduction of the dioxide to the sesquioxide with zinc and hydrochloric acid, and then titrating back with an oxidizing agent, such as potassium permanganate.

Ore Assay

The estimation of titanium in minerals has been described by Ohly, and his procedure for rutile exemplifies the method used by many assayers. The rutile is finely powdered and fused with 3 times its own weight of potassium carbonate, the fusion-mass being allowed to cool and then treated with water to remove the alkaline silicates. The insoluble potassium titanate and ferric oxide remain behind. The residue is washed with cold water and dissolved in hydrochloric acid.

After diluting with water and heating to the boiling point, all the titanium precipitates out as the metatitanate. It usually has a yellowish tinge due to the presence of a small amount of iron which it carries down. In order to remove this impurity, the precipitate is filtered off, washed with ammonium chloride, and dissolved in sulfuric acid. After dilution with water and long boiling, it is reprecipitated as before. The iron is removed at this point. This procedure also allows the separation of aluminum, beryllium, yttrium, and thorium.

Titanium may be assayed by fusing the substance to be tested with about 6 times its own weight of potassium bisulfate until a clear fusion-mass is obtained. This is then dissolved in

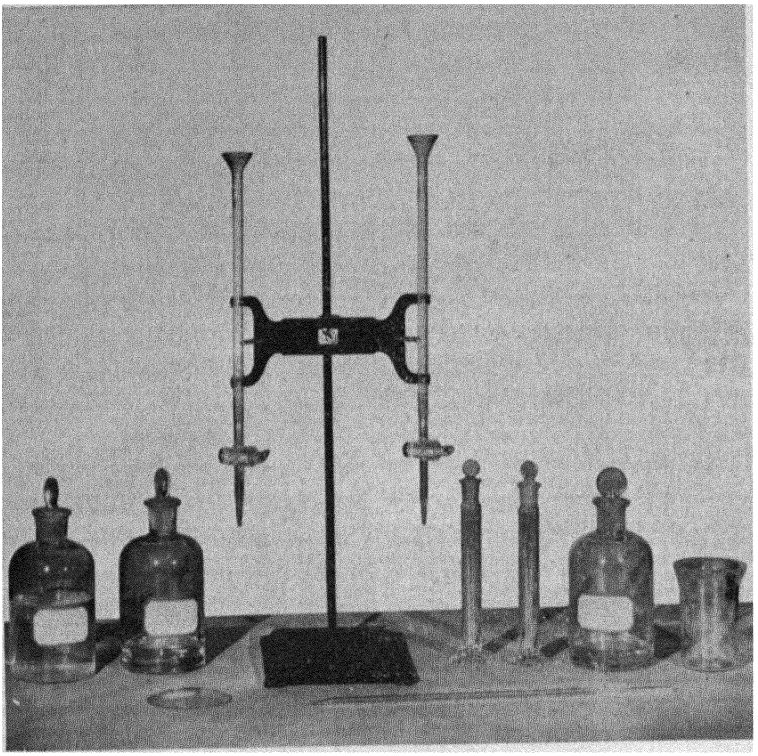


FIGURE 6
Apparatus for titanium analysis (courtesy of General Electric Research Laboratory).

water which has been acidulated with sulfuric acid. Metatitanic acid precipitates out; the silica is not attacked by the potassium bisulfate and remains as an insoluble residue.

Instead of potassium bisulfate, potassium bifluoride may be employed, the fusion-product being dissolved in dilute hydrochloric acid. This results in the formation of potassium fluotitanate, which is only slightly soluble in cold water. It is col-

lected on a filter and purified by repeated recrystallizations from hot water. On addition of ammonium hydroxide, hydrated titanium oxide forms, which may be reduced to the anhydride by ignition. Silica and traces of silicates may be removed by decomposition with hydrofluoric acid. Sulfuric acid is added to prevent titanium from being lost when silicon fluoride volatilizes.

Titanium may be detected in the presence of vanadium if dihydroxy maleic acid[32] is added to the hydrogen peroxide. Both elements give an orange color with hydrogen peroxide, but the addition of dihydroxy maleic acid inhibits the color formation with vanadium and not with titanium.

Tests

In the Dobrolyubskii test for titanium, to the solution of the sample in 6 N hydrochloric acid there are added 3 to 4 drops of 0.025 per cent methylene blue solution and a small piece of zinc. If titanium is present, the solution will be decolorized within 4 minutes. Ferrous, uranyl, and manganous ions do not interfere. It is claimed that as little as 0.05 gamma of titanium can be detected in a drop of solution. A blank test should be run to establish the rate of decolorization without titanium.[33]

Feigl[34] has developed the following test for titanium. To 50 or 150 cc of the solution to be tested dilute sodium hydroxide, containing a small amount of sodium carbonate, is added until the solution is alkaline. It is then heated to boiling, filtered, and allowed to come in contact with a drop of benzidine acetate solution. The formation of a blue color indicates the presence of titanium. Manganese, cerium and cobalt also give the reaction.

In another test for titanium developed by the same investigator,[35] 10 cc of solution are made 1N with hydrochloric acid, a drop of 1 per cent zirconium solution and 10 drops of 20 per cent arsenic acid are added, and the whole boiled for a short time. The precipitate formed is separated and washed by cen-

trifugation until all colored components have been removed. A drop of concentrated sulfuric acid is added to a small quantity of precipitate, which dissolves with the aid of gentle heating. On cooling, and adding a drop of hydrogen peroxide, a yellow color develops when the test is positive, as little as 1 gamma titanium evoking the reaction.

Titanium may be detected in the presence of other metals by saturating filter paper with 10 per cent tannic acid solution, adding a drop of 20 per cent antipyrine solution, and then a drop of the solution to be tested. Formation of a red spot indicates titanium, as little as 1 part in 250,000 parts of solution producing the reaction.[36]

This test is very effective since it may be conducted in the presence of Fe, Cr, Al, Co, Ni, Mn, Zn, Hg, Pb, Cu, Cd, Bi, and Zr. The procedure is to treat the red spot with 1:4 sulfuric acid to remove any other coloration except the red-brown of titanium. Molybdenum also reacts by giving a green-brown spot.

Solutions containing trivalent titanium ions give vari-colored precipitates with potassium thiocyanate, ferrocyanide, and ferricyanide. Sodium acetate and sodium formate give colored solutions with titanium at room temperatures, and upon heating precipitation occurs. A saturated sodium oxalate solution produces a crystalline precipitate. Normal tartrates give precipitates which are soluble in an excess of reagent.[37] An aqueous solution containing titanium ions gives a yellow-to-orange coloration when hydrogen peroxide is added.[38]

A convenient microchemical test for small bits of solid titanium compound is to fuse the sample with potassium bisulfate in a platinum loop, decompose the resulting bead in a solution of 0.1 to 0.2 g of salicylic acid in 20 to 30 drops of concentrated sulfuric acid. If titanium is present the mass becomes red. In this test results may be enhanced if fluorochemical analysis is used in conjunction with white light examination, since a fluorescent substance, salicylic acid, is used.

The test cannot be employed in the presence of molybdenum, vanadium, or tungsten.[39]

Another reagent for titanium analysis consists of sodium potassium tartrate solution which has just been tinted with fresh indigo solution. A hydrochloric acid solution of titanium decolorizes this reagent, the color being restored on aeration. As little as 40 gammas of titanium can be detected. The test is claimed to be more sensitive when methylene blue is used without the Rochelle salt.[40] This is in accordance with the test of Dobrolyubskii.[34] A deep wine-red coloration forms when titanium solutions are added to morphine in sulfuric acid.[41]

A reagent useful for detecting titanium consists of alcoholic acetic acid saturated with thymol and acidified with sulfuric acid. When titanium ions come in contact with the colorless reagent a pale red coloration develops. The intensity of color is a function of the amount of titanium, as little as 100 gammas of titanium dioxide being detectable.[42] The Moir test, described in chapter 4, is adaptable to titanium.[43] When titanium solutions are treated with a solution of ammonium oxalate and then with zinc and sulfuric acid, a yellow color (changing to orange) forms.

Titanium, thorium, and zirconium form lakes with alizarin (1,2-dihydroxy anthraquinone). This is the basis for sensitive tests for these elements. Filter paper is saturated with an ethanolic solution of the dye and allowed to dry. A drop of the solution to be tested is placed on the paper and then held over the mouth of a bottle containing ammonium hydroxide. A red-violet coloration appears with as little as 1 part titanium in 166,000, being more visible when dried. Zirconium gives a raspberry-red color which is sensitive to 1 part in 103,000, and thorium gives a violet lake which is sensitive to 1 part in 125,000.[44]

Trivalent titanium ions produce a yellow-orange coloration with oxalic acid or pyrocatechol solutions. In extremely high dilutions the color is yellow. This reaction is about 15 times

more sensitive than that with hydrogen peroxide. As little as 200 gammas of the element may be detected in 1 l of solution when in the form of the trichloride.[45] Similarly, when titanium sulfate is brought into contact with chromotropic acid, a deep-brown color forms.[46] As little as 5 gammas of titanium dioxide in a drop of solution can be detected. The test is not as sensitive with stannous chloride present, but it must be added to prevent interference by uranyl and ferric ions.

Zirconium and Hafnium

History

Zirconium

Although the fire of the beautiful zircon crystals was known to the ancients, it was not until 1789 that the German chemist Klaproth demonstrated the real composition of zircon. He proved that it was not composed of alumina and silica as had been supposed, but contained a new earth, zirconia, the oxide of zirconium. However, the isolation of the metal zirconium was a very difficult problem. A number of the foremost chemists, including Davy, Vauquelin, Berzelius and Moissan, tackled the problem of isolation, but the result in each case was a relatively impure metal. It was not until 1914, 125 years after Klaproth's discovery, that the Hollanders, Lely and Hamburger obtained 100 per cent metallic zirconium. They reacted $ZrCl_4$ with sodium metal in a high-pressure steel bomb. Compressing the metallic laminae into a rod, they produced from it zirconium metal wire with a mirror-like surface.[47]

However, Lely and Hamburger were not aware of the fact that closely associated with and very similar to zirconium was another metal, hafnium, which was not definitely isolated and identified until 9 years later.[49]

FIGURE 7
Fine structure of zirconium containing silicon as an impurity, magnified 500X (courtesy of Westinghouse Research Laboratories).

Hafnium

The exact point at which the history of hafnium begins is rather vague. As early as 1845 the chemist Svanberg announced to the Swedish Academy of Science that zircon was made up of two distinct earths. To the other element he gave the name *norium*. Subsequently, several chemists made thorough investigations in order to decide the composition of zircon, and after failing to verify Svanberg's conclusion, pronounced it erroneous.

Several years later, Sorby was led by spectroscopic evidence to conclude that zircon was composed of 2 elements. He called the new element *jargonium*, a term derived from the zircon mineral, jargon. Still later, Forbes was led to think as Sorby did, but as both investigators were unable to isolate their element, they abandoned the investigations and ascribed the peculiar dark bands in the spectrum of zircon to uranium.

It was not until 1911 that more serious investigations indi-

cated the possible existence of a new element in zirconium ores. Urbain used spectrochemical and other methods of analysis and arrived at such a conclusion. In 1922 Dauvillier substantiated this work. However, the results were thought to be faulty and due to impurities of various kinds. But later in 1922, and in the early part of 1923, Coster and Hevesy examined a number of zirconium minerals and demonstrated that some of them contained up to 30 per cent of the oxide of a new element. All zirconium ores contained traces of the new element, the average content being about 3 per cent. These investigators named the new element hafnium and by X-ray spectroscopy established its true place in the periodic table and showed that its atomic number was 72. Interest in hafnium has been relatively great in recent years. Hevesy wrote a book on the subject in 1927.[48]

When, in 1914, the English physicist Mosely discovered the relationship which exists between the X-ray spectrum of an element and its atomic number, there were seven unfilled spaces in the periodic table: element 43, masurium; 61, illinium; 72, hafnium; 75, rhenium; 85, ———; 87, ———; and 91, protoactinium.[49]

Mineralogy of Zirconium and Hafnium

Zirconium and hafnium are found associated with other elements in small, widely diffused quantities. The chief source of zirconium is the mineral zircon, $ZrSiO_4$, which is a very common accessory constituent in all classes of igneous rocks. Zircon is especially common in the more silicic rocks, such as granite, syenite, and diorite. It is also characteristic of the nepheline syenites. Second in importance to zircon is the mineral baddeleyite, ZrO_2. Extensive, as yet only partially developed deposits occur in the Pocos de Caldas region of Brazil. Baddeleyite crystallizes in the monoclinic system, but the silicate, zircon, crystallizes in the tetragonal system.

Zirconium

Commercial sources of zirconium are virtually limited to alluvial deposits, chiefly, concentrated black-sand accumulations, which are available in relatively few places in the world. Zircon is the principal zirconium mineral present in these sands. While zirconium is classed as a rare metal, it has been generally agreed among investigators that at least 0.02 per cent of the crust of the earth is composed of zirconium. The element appears to be more abundant in the crust of the earth than nickel, copper, zinc, and lead, which are so-called "common metals." The fact that zirconium minerals are so widely scattered and that zirconium metal is so costly to prepare, places zirconium in the rare metal category.

A growing demand for zirconium has stimulated the search for new deposits during the past decade. A number of important discoveries of zirconium deposits have recently been made in Australia and India. The black sands of the Pacific coast of the United States have long been investigated for their zirconium and titanium content, and it is possible that these deposits can be worked in an economical manner with the development of improved methods of recovery. Rutile and ilmenite, sources of titanium, are frequently recovered along with zircon. Extensive deposits of zircon and baddeleyite in Brazil have recently been described.

Pure zircon contains 32.8 per cent silica and 67.2 per cent zirconium. It is characterized by a high specific gravity (about 4.69) and a hardness of 7.5. Distinct crystals are found in many igneous rocks. There are several varieties and alteration products of zircon, including hagatalite, oyamalite, crytolite, aerstedite, malacon, and orvillite. The rare earths and 4 per cent or more of hafnium oxide are found in some varieties of zircon.

Gem varieties of zircon are comparatively rare, and most of these originate in the gem-bearing gravels of Ceylon. Gem

zircon occurs in a variety of colors. Heat treatment is widely used to improve the color of gem-quality zircon. Zircon has a high index of refraction, and the colorless gem has 86 per cent of the "fire" of the diamond.

Hafnium

Hafnium, like zirconium, is never found in the free state, although it is widely distributed in nature and is invariably associated with zirconium. This fact necessitates the revision and correction of all old data on zirconium because nearly all zirconium salts are contaminated with from 1 to 5 per cent hafnium. A good example of this is given in the fluorescence of zirconium minerals and compounds which have been shown by spectographic examination to contain hafnium which is assumed to be the activator in a phosphor-like system.[50]

Lee [51] gives a thorough discussion of the subject. He points out that the examination of some 70 minerals, mostly varieties of zircon, shows amounts of hafnium, calculated as the oxide, ranging from 0.2 to 15 per cent. The probable concentration of hafnium in the earth's crust is 1 part in 100,000.

Physical Properties

Zirconium

Pure zirconium is a ductile metal with a distinct crystalline structure and a white metallic luster. The melting point of zirconium is 2130°C. When a filament of zirconium is heated in air the surface becames superficially oxidized. It has been mentioned in the literature that specimens of zirconium are brittle and easily broken by light pounding with a small hammer, but the metal made by the van Arkel and de Boer procedure is malleable. The larger granules which have been prepared can also be hammered.

Zirconium readily alloys with many metals, and in most instances the product is obtained simply by heating the con-

stituents together. Zirconium dissolves in copper at its melting point, but not in silver. Zirconium can be welded to nickel, but at higher temperatures molybdenum and tungsten provide better contact metals.

In steel, zirconium acts as a deoxidizer, denitrifier, and desulfurizer. It increases the toughness and tenacity of steel, best results being obtained when the zirconium content is equal to or less than 0.15 per cent, and in few cases, it exceeds 0.35 per cent. Tests have shown that nickel-chromium steel of 16 mm thickness, and nickel-zirconium steel of 10 mm thickness have equal resistance to passage by rifle bullets.

Hafnium

A comparison of the physical data on zirconium and hafnium will be found in table 6 in this chapter. It will be noted from this table that the melting and boiling points of these elements are close, and that the specific gravity (13.3) of hafnium is over twice that of zirconium (6.5). Both zirconium and hafnium are bi- and tetravalent and both are mixtures of 5 isotopes. Both crystallize in the hexagonal system. Hafnium is heavier than lead. When pure it is very ductile. Its resistivity is 30×10^{-6} ohm as against 41×10^{-6} ohm for zirconium. The temperature coefficient of resistance of the two metals is practically the same, 440×10^{-5} per 1°C.

Chemical Properties of Zirconium

Pure zirconium is very resistant to the action of most chemicals, including hydrochloric and nitric acids, but is attacked by hydrofluoric acid. The metal burns in air at high temperatures and, in fact, very thin filaments can be lighted with a match. At high temperatures it combines with nitrogen, at dull red heat with chlorine, and at about 371°C with hydrogen. Zirconium forms compounds with silicon, carbon, boron, and phosphorus. These impurities must be avoided in manufacturing the metal.[52]

Zirconium Compounds

As has been pointed out, zirconium is always closely associated in nature with hafnium. In fact, the two are so closely associated that an investigation of the properties of zirconium often involves the study of a mixture of zirconium and hafnium. Chemically, the compounds of zirconium bear a close resemblance to the compounds of thorium, titanium, germanium, and silicon, this being evident from their proximity in the periodic table. Zirconium has a valence of either two or four in all its compounds.

Aluminum forms compounds with zirconium, which have a high melting point and low rate of evaporation. Therefore, when zirconium and aluminum are brought together in a heated chamber, an alloy is produced. This alloy, incidentally, is characterized by its high ductility.

Zirconium forms an important oxide, ZrO_2, and other compounds such as the halides, the silicate, nitrate, sulfate, and so on. Unlike thorium and yttrium, zirconium does not form a precipitate with hydrofluoric acid.

Ammonium carbonate added to a zirconium salt yields a white flocculent precipitate of the basic carbonate, which dissolves in an excess of potassium carbonate or potassium bicarbonate. Ammonium hydroxide and ammonium sulfide precipitate zirconium as a white, flocculent hydroxide, which is insoluble in an excess of reagent, and insoluble in sodium hydroxide.

With oxalic acid, the zirconium oxalate forms. It is insoluble in an excess of regeant, soluble with difficulty in hydrochloric acid, easily soluble in an excess of ammonium oxalate.

Zirconium sulfate is produced by treating the carbonate, hydroxide, or oxide with concentrated sulfuric acid. After driving off the excess of H_2SO_4 at a temperature below 400°C, the normal sulfate, $Zr(SO_4)_2$, remains. On contact with water, heat is evolved and a tetrahydrate is formed, which is slowly dissolved in water. There are a number of complex salts of the zirco-sulfuric acids.[58]

There is only one well defined zirconium nitrate, i.e., $ZrO(NO_3)_2.2H_2O$, zirconyl nitrate dihydrate.

Zirconium phosphate is practically insoluble in all solvents except hydrofluoric acid. The hafnium phosphate is even more insoluble.

Zirconium chloride, $ZrCl_4$, forms well-shaped white needles that sublime at 350°C. It fumes in air, since it hydrolizes very easily. With ammonia it forms an addition compound, $ZrCl_4.8NH_3$.

Upon hydrolysis, colorless needles of $ZrOCl_2.8H_2O$ are formed. In aqueous solution this oxychloride gives an acid reaction.

Zirconium bromides, iodides and fluorides are all well known.[52]

Zirconium oxide, ZrO_2, is one of the most important compounds of zirconium because of its stability at high temperatures.

The oxide has acidic qualities behaving like thorium oxide toward bases. With weak acids zirconium oxide exhibits weak basicity and forms basic salts, such as carbonates and oxalates. With strong bases it shows acidic properties, and like the oxide of titanium it forms zirconates. The important double salts of zirconium are represented by the formula M_2ZrN_6, where M is an alkali metal, and N may be a halide or nitrate. Thus, K_2ZrF_6 yields zirconium metal upon reaction with sodium, and the compound itself has been used as a scavenger in steel.

Extraction of Zirconium from Ores

There are several methods for separating zirconium from its ores. For example, an ore containing 47.5 per cent zirconium oxide and 30 per cent silica is heated with sufficient calcium oxide, the proportion used being about 10 parts ore to 7 parts calcium oxide, in an electric furnace using about 12,000 kilowatts per hour for every 1000 kg of zirconium oxide. The fusion-product is treated with hydrochloric acid to

make zirconium oxychloride, or with sulfuric acid to produce the sulfate.[54]

Zircon may be used as the source of zirconium compounds. It is thoroughly pulverized and fused with potassium bifluoride. The potassium fluozirconate, K_2ZrF_6, formed can be separated from the insoluble fluosilicate by means of hot water acidulated with hydrofluoric acid. The zirconium is separated from the filtrate by precipitation with ammonium hydroxide and filtering. Zircon or baddeleyite ores may also be treated by heating with fused potassium hydroxide or other alkalis and the residue treated with sulfuric acid to dissolve the zirconium and silicon. When the solution is cooled to about 47°C, the zirconium compounds precipitate.[55]

In another method for obtaining zirconium salts, the ore is fused with an alkali. The residue, after leaching and ignition, consists of 90 per cent zirconium oxide. The moist residue may be purified by stirring it into a paste with ammonium binoxalate, diluting with water, removing the insoluble material by filtration, and crystallizing out ammonium zirconyl oxalate from the filtrate. Upon ignition of this compound large, pure crystals of zirconium oxide are obtained.

Baddeleyite ores may be decomposed by fusion with potassium bisulfate or by heating with concentrated sulfuric acid. From the solution obtained, the phosphate is precipitated with sodium biphosphate. The phosphate is dissolved in ammonium binoxalate and the ammonium oxalate separated from ammonium zirconyl oxalate by crystallization. There is an alternative treatment for the sulfate solution obtained just before the phosphate precipitation. It can be partially neutralized and evaporated to from 8 to 10 per cent zirconium oxide, and then treated with potassium sulfate and oxalic acid. The potassium zirconyl oxalate formed is separated from the mother liquor, purified by recrystallization from hot water, and decomposed with an alkali hydroxide or carbonate.[56]

Zirconium may be recovered from its ores by fusing the ore with calcium oxide and calcium chloride (or fluoride) and treating the fusion-product with less than the theoretical amount of hydrochloric acid required to combine with all the other bases. The concentrated solution is filtered and treated with an excess of concentrated hydrochloric acid in order to precipitate zirconium oxychloride.

The separation of zirconium from iron and titanium has received considerable attention from chemists.[57] It may be accomplished by the action of water on an ether solution of the chlorides, by the action of gaseous hydrogen chloride and chlorine at about 200°C upon the mixed oxides, by treatment with phenylhydrazine, or by the action of sulfurous acid on neutral solutions.

Separation of titanium from zirconium may be achieved by boiling a solution of the two metals with dilute sulfuric acid and acetic acid to precipitate the titanic acid. The solutions can be treated with hydrochloric acid and zinc until the titanium is reduced to the sesquioxide, and then potassium sulfate added, the zirconium potassium sulfate precipiating out. Another method of separation is to add hydrogen peroxide and sodium phosphate to the solution. The basic phosphate of zirconium precipitates out.

Separation of Zirconium and Hafnium

Early investigators of the zirconium-hafnium combination were convinced that it would eventually have commercial importance and, as a result, the patent literature gives more information on the separation of the elements than do the reports in scientific journals.

Separation of zirconium from hafnium may be brought about by the action of water on a sulfuric acid solution of the phosphates of the two elements.[58] Alternatively, a mixture of the phosphates with hydrofluoric acid is subjected to fractional

decomposition by the addition of boric acid. The mixture of hafnium and zirconium phosphates precipitated is richer in hafnium than the original mixture.[59]

Coster and Hevesy have patented several methods for separating zirconium from hafnium.[60] Oxychlorides or other halogen compounds of hafnium and zirconium are subjected to fractional crystallization from a hydrochloric acid solution. In a second method, a mixture of the dissolved phosphates, containing free hydrofluoric acid, is fractionally precipitated on the addition of sulfuric acid, boric acid (or other boron compounds), or the salts of aluminum, tin, tungsten, molybdenum, chromium, vanadium, tantalum, columbium, beryllium, or silicon in solution.[61]

Preparation of Zirconium Metal

Berzelius, in 1824, was the first to prepare crude zirconium metal by reducing zirconium fluoride with potassium in a closed vessel. The following reaction took place:[62]

$$ZrF_4 + 4K = Zr + 4KF$$

Later investigators reduced the double salt, $KFZrF_4$, with sodium, aluminum, or a mixture of calcium and sodium. Zirconium oxide, ZrO_2, can be reduced to the metal with a mixture of magnesium and sodium.[63] Zirconium chloride reduced with sodium metal (see under ductile zirconium) produces ductile zirconium. Zirconium oxide is reduced by atomic hydrogen, but not by molecular hydrogen.

Ductile zirconium is best prepared by thermal reduction or decomposition of volatile zirconium halogens. Van Arkel and de Boer proceed as follows:[64]

A thin zirconium wire is heated electrically to 1400°C in an enclosed atmosphere of zirconium iodide, ZrI_4. At this white-hot temperature, the iodide is broken down according to the equation $ZrI_4 \rightarrow Zr + 2I_2$, and pure zirconium is deposited on the heated wire. After a few hours, the wire has increased to several millimeters in diameter. The rods thus produced are

very ductile and readily drawn or rolled. A tungsten wire may be used instead of the zirconium wire. To prepare the ZrI_4 it is convenient to start with purified ZrO_2 and convert it to the chloride:[65]

$$ZrO_2 + CCl_4 + Cl_2 = ZrCl_4 + CO_2 + Cl_2$$

The $ZrCl_4$ is then reduced with sodium metal. The ductile zirconium granules thus produced are introduced into the van Arkel-de Boer reaction vessel for conversion to the iodide. Upon decomposition of ZrI_4 on the hot filament, the liberated iodine reacts with the zirconium metal powder to form fresh ZrI_4.

This ductile zirconium of van Arkel and de Boer is used in making the small funnel-shaped spinnerets for rayon manufacture.

The whitish, massive zirconium resembles antimony. Blue-black zirconium powder, prepared by decomposing sodium zirconate with iron, differs from the massive, compact zirconium in both chemical and physical properties. The blue-black zirconium powder burns brightly in air to the oxide, but the massive form does not. The powdered zirconium metal is oxidized by fused alkali carbonates and chlorates but is only slightly attacked by acids.

Technology of Zirconium

During the past few decades, zirconium has become important as a secondary metal for many kinds of industrial processing. The metallurgical fields, in particular, have realized benefits from zirconium, and at present the search continues for new applications of this element.

Gem Zircon

Known to the gem trade for many years, zircon remained in obscurity until about 20 years ago, when it first gained popular attention. Since then it has become an important semi-precious

gem stone. Zircon is available in several colors, including blue-green, yellowish, brown, and reddish-orange. Colorless zircons have a dispersion about 86 per cent that of the diamond.

Small zircons have very little value, but stones of good color and quality weighing over 5 carats bring premium prices. Practically all of the blue-green stones have been developed by heat treatment. By careful heat treatment some inferior stones can be greatly improved in color. However, the color of heat-treated zircon may not be permanent, tending to fade slowly when exposed to sunlight. The color may be restored by another heat treatment.

Zirconium oxide is a valuable refractory and opacifier (see under zirconium oxide).

Ferrous Metallurgy

In ferrous metallurgy, zirconium is of distinct importance. It acts as a deoxidizer, denitrifier, and desulfurizer. Zirconium also imparts to steel toughness, tenacity, resistance to wear, and resistance to corrosion. Best results are obtained in concentrations of from 0.15 to 0.35 per cent zirconium. When from 0.08 to 0.10 per cent of zirconium is added to steel, an improvement in grain structure is noted.[66]

A typical nickel-zirconium steel contains 0.40 per cent carbon, 1 per cent manganese, 1.5 per cent silicon, 2 per cent nickel, and 0.34 per cent zirconium. Zirconium, when added as ferro-zirconium (containing 30 to 35 per cent zirconium), appears to produce the best results.

Chrome, vanadium, nickel, manganese, and other special steels have enhanced physical qualities when zirconium is added. An alloy suitable for castings, valves, dies, cutlery, etc., is made up of 8.75 per cent chromium, 3 per cent nickel, 1 per cent copper, 1.5 per cent silicon, 0.2 per cent carbon, 0.5 per cent titanium, and 0.75 per cent zirconium.[67]

Zirconium-manganese steel, containing from 1 to 2 per cent manganese, less than 2 per cent carbon, and 0.15 per cent zir-

conium, has a high resistance to shock. The zirconium content is variable and may reach 0.5 per cent.[68]

Zirconium added to chrome steel in quantities from 1.59 to 2.0 per cent prevents brittleness.[69] A ferrous alloy containing zirconium may be used for wrought articles, such as tubing.[70] It contains 10 to 20 per cent chromium and 0.008 per cent or more zirconium, depending upon the working properties desired.

Non-ferrous Metallurgy

There has been considerable investigation of the non-ferrous metallurgy of zirconium. Cast nickel-silicon bronze and other non-ferrous alloys benefit by additions of zirconium. Several zirconium-tungsten alloys have been developed. They are useful in the vacuum tube industry. A layer of zirconium on tungsten is formed by the thermal decomposition of a zirconium compound, such as the oxychloride. The zirconium and tungsten are heated in an inert atmosphere, and alloying takes place between the two metals.[71]

In the preparation of alloys with high melting points, 20 per cent or more molybdenum, 5 per cent zirconium, up to 80 per cent tungsten and 0.5 to 4 per cent carbon can be employed. The tungsten and the molybdenum can be replaced by tantalum. As much as 20 per cent zirconium can be added.[72]

Saklatwalla [73] has prepared an alloy of copper, containing from 14 to 16 per cent zirconium, which has properties similar to those of some beryllium alloys. About 6 per cent aluminum and vanadium, 40 per cent silicon, and the remainder iron, go into the composition of this alloy. It is claimed to be superior for steel refining, because it overcomes some of the disadvantages of adding each alloy or pure metal separately.

Other Uses

Zirconium metal finds use in photoflash bulbs, radio transmitter tubes and other vacuum tubes, in spot welding, and as

a primer in ammunition. Zirconium can be introduced into welding rods for electric welding with good results. Sheet zirconium goes into the make-up of rayon spinnerets.

Zirconium has the unusual combination of high corrosion resistance and a great power of gas absorption. At 500 to 860°C the metal absorbs large volumes of hydrogen, and at higher temperatures it absorbs oxygen, carbon monoxide, carbon dioxide, and many other gases. Specialized applications arise because of this property. For example, pure zirconium is introduced into the evacuated part of a radio tube to act as a "getter" for residual and occluded gases given off during operation.[74]

Fink [75] has developed a method for producing tungsten in ductile form. By incorporating into a slug of tungsten metal about 1.4 per cent zirconium and heating in hydrogen, a ductile product is obtained. The zirconium, having a high affinity for hydrogen at elevated temperatures, reacts with the intercrystalline impurities. The filament is comparatively soft and non-sagging. This process may be extended to other metals which are difficult to obtain in filament form.

Zirconium oxide, ZrO_2, is a valuable refractory for lining furnaces and for making glass and porcelain heat-resistant. It can also be used to face fire-clay articles. As a refractory cement and furnace lining, it has a melting point of about 2500°C. It is characterized by a low coefficient of expansion, low thermal conductivity, and very high resistance to corrosive slags and gasses. Zirconium oxide cement is valuable as an insulator in tungsten-wound alundum tube resistor furnaces. Hydrogen, or a mixture of 25 per cent hydrogen and 75 per cent nitrogen, is used as the protective gas for the tungsten wire. A mixture of 50 per cent high- and 50 per cent low-burned zirconium oxide is employed.[76]

Zirconium oxide can be added to glass to increase its resistance to chemical reagents. In studying the relationship between chemical composition and the resistance of glass to var-

ious chemicals, it was found by Dimberly and Turner [77] that additions of zirconium oxide up to 6 per cent gave products with the greatest resistance to alkaline solutions. Sodium dioxide-zirconium dioxide-silicon-oxide glasses showed great durability. Zirconium oxide can be added in amounts greater than 8 per cent without influencing the transparency of glass. Zirconium compounds lower viscosity, annealing temperature, density, and thermal expansion. They give a product which has greater resistance to water, certain acids, and alkalis.

There is an increasing application of zirconium oxide in the manufacture of ceramics, enamels, and glaze frits. Zirconium-processed enamels and glazes are non-poisonous. The same opacity is obtained with 2 per cent zirconium as with 6 per cent antimony oxide. Zirconium oxide was the basis of the old Nernst glower.

There are, according to de Boer, at least three crystal modifications of ZrO_2. In this respect it resembles SiO_2 and TiO_2. The melting point of pure, white ZrO_2 is 2680°C. It is a good insulator for heat and electricity. After ignition it is practically insoluble in all acids, except hydrofluoric acid. It is slowly dissolved by fused alkalis. Heating it with carbon will yield the carbide, ZrC; heating it with carbon in the presence of chlorine will yield $ZrCl_4$.

Zirconium Analysis

Ore Assay

In the quantitative determination of zirconium in minerals, the sample is heated to redness and dropped into water. The substance so treated is then finely pulverized and 1 g of it mixed with 4 g of sodium carbonate. This mixture is fused, together with a small amount of potassium nitrate, in a platinum vessel until fully metathesized. The fusion-product is treated with water, hydrochloric acid, and a few drops of nitric acid, and the silica is removed in the usual fashion.

Ammonium hydroxide is added to the filtrate from the silica separation to precipitate hydrated zirconium oxide, aluminum hydroxide and ferric hydroxide. After settling for several hours, the precipitate is filtered off and washed. It is then dissolved in hydrochloric acid and the solution diluted with water.

Saturated sodium carbonate solution is added and the solution is allowed to cool. It is then decolorized with sodium thiosulfate and boiled until sulfur dioxide ceases to be given off. The precipitate of hydrated zirconium oxide is filtered off, washed well with water, ignited, and weighed as the oxide.

Detection and Analysis

A white hydrogel forms when a solution containing zirconium is strongly acidified with nitric acid, a few drops of sodium phosphate solution are added and the solution warmed. The presence of sulfuric acid inhibits formation of the precipitate.[78] Feigl and Rajmann[79] have developed a test for zirconium. To 10 cc of the test solution, made 2 N with hydrochloric acid, 12 drops of acidic 4 per cent titanium solution and 1 cc of 20 per cent arsenic acid solution are added. This solution is boiled for several minutes, filtered, and washed with the aid of the centrifuge. The precipitate so obtained is moistened with 1 drop of a mixture of 10 parts concentrated sulfuric acid, 1 part 30 per cent hydrogen peroxide, and 10 parts water. Solution is insured by gentle warming. It is diluted with 1 drop of water and tested for zirconium with alkyl azoarsenic acid test paper. As little as 1.25 gammas of the element are detectable in this way.

An aldehyde reagent for the detection of thorium and zirconium is made by dissolving 38 g of pyrogallol and 36.3 g of formanilid in anhydrous ether, and treating with 15.2 g of phosphorus oxychloride. After standing for 18 hours, the solution is filtered through a Büchner funnel and the precipitate recrystallized from alcohol containing sodium chloride.

While warming, decompose with sodium hydroxide solution in a stream of hydrogen, then acidulate and extract with ether. The resulting aldehyde is purified through the bisulfite compound.

This reagent becomes bright yellow with thorium nitrate and thorium sulfate. On standing, precipitation occurs and a dirty yellow precipitate is thrown out of the solution, which then becomes colorless. Zirconium compounds behave similarly, whereas those of cerium form a brown-yellow color which is resistant to boiling.[80]

A good reagent for zirconium is *p*-dimethylamino azobenzene arsonic acid. When a drop of the solution to be tested is placed on filter paper saturated with the reagent and then immersed in warm 0.2 N hydrochloric acid solution, a brown color forms. It is claimed that 100 gammas of the element may be detected.[81]

Cupferron ($C_6H_9O_2N_3$) may be employed in sulfuric acid solution for separating zirconium from aluminum, chromium, uranyl, and boron. Titanium, thorium, cerium, iron, vanadium, columbium, tantalum, and tungsten must be absent. If these elements have been eliminated, together with silicon, zirconium may be determined quantitatively.[82]

A reagent for zirconium consists of a 1 per cent ethanolic solution of β-nitroso-α-naphthol in hydrochloric acid. With zirconium it gives a red coloration which is the basis for a colorimetric estimation of the element.[83] However, many elements interfere.

Zirconium forms a red lake with alizarin, this test being described in the section on titanium analysis.[84] With an aqueous solution of *iso*dipropylamine, salts of magnesium, aluminum, zinc, zirconium, tin, cadmium, antimony, bismuth, and lead, all yield white precipitates which are not soluble in an excess of reagent.

Arsenic acid as a reagent for zirconium analysis has been discussed fully from both practical and theoretical aspects by

Feigl.[85] Zirconium arsenate is precipitated as a white solid from nitric or hydrochloric acid solutions. The activity of the arsenic acid is retained by its organic derivatives, and consequently these reagents have been developed for the purpose of detecting and estimating zirconium. Table 11 lists some of these compounds and their limit of sensitivity in saturated aqueous solution on 2 cc of an acid zirconium chloride solution.

TABLE 11

SENSITIVITY OF THE ZIRCONIUM-BINDING GROUP *

Arsonic acid Derivative	*Limit of Identification (Gammas)*
Arsanilic acid	60
Acetarsanilic acid	16
Nitroarsanilic acid	24
Dichloroarsanilic acid	24
p-Tolylarsonic acid	24
m-Benzarsonic acid	16
Salicylarsonic acid	16
Biphenylarsonic acid	32
3-Chlorarsanilic acid	24

* Feigl calls this the *zirconium-binding* group and ascribes the activity specifically to the $AsO(OH)_2$ group.[85]

Determination of Zirconium in Steels

Cunningham and Price[86] recommend the following procedure for the determination of zirconium based on the rapid precipitation of $Zr(HPO_4)_2$ in the presence of titanium, aluminum, tungsten, molybdenum, chromium, vanadium, uranium, cobalt, nickel, copper, tin, arsenic, manganese, tantalum, columbium and silicon—all of which are found in some types of plain carbon or alloy steel.

Five or 10 g of the steel drillings are treated with 40 to 60 cc of HCl (specific gravity 1.19) at 80°C. Then 8 to 15 cc of hydrogen peroxide (30 per cent solution) are added, heated for 2 minutes and diluted with warm water to 350 cc. Next, ammonia is added until a permanent precipitate is formed. This

is carefully redissolved with HCl, adding sodium sulfite to reduce all the iron to the ferrous state. Then 8 to 10 g of diammonium phosphate are added. The solution is stirred vigorously for 10 minutes and allowed to stand at 70°C for ½ hour. Finally, the precipitate is ignited in a porcelain crucible to ZrP_2O_7.

Simpson and Schumb [87] found that zirconium can be satisfactorily determined in steels by precipitation from dilute HCl solution with selenious acid in the presence of hydrogen peroxide, and ignition of the precipitate to ZrO_2.

Hafnium Analysis

In general, the reactions given for zirconium can be applied to hafnium also. However, in some cases this may not hold strictly true.

When the acetyl acetonate of hafnium is dissolved in carbon disulfide, a red coloration develops after standing for several hours in the cold. The color forms more quickly when the solution is heated. Zirconium also gives this reaction, but thorium does not. The acetyl acetonate is prepared from zirconium oxynitrate or hafnium oxychloride, acetyl acetone and sodium carbonate solution. The product is recrystallized from alcohol or acetyl acetone.[89] One distinction between hafnium and zirconium is that the oxalate of hafnium is soluble in excess oxalic acid, but the oxalate of zirconium is not.

Thorium

History

Thorium was discovered by Berzelius in 1829. While working with a black mineral now known as thorite, from the island of Lövö, Norway, he came upon a new earth which he called *thoria,* after the Swedish god Thor, son of Odin.[90] In 1851 Bergmann demonstrated its presence in the mineral orangite.

The radioactive properties of thorium were observed in 1898 by Marie Curie and Schmidt.

Mineralogy

Thorium is found in at least 100 minerals, in amounts ranging from traces up to about 70 per cent. The element is not found in the native state, but its oxide comprises one of the most important of thorium minerals, thorite. De Ment and Dake [91] have described about 180 radioactive minerals, many of which contain thorium. The reader is referred to this work for a more detailed description of the ores. The radioactive minerals have been tabulated and described in a series of papers in *The Mineralogist*.[92] Many of the minerals given in table 15, Chapter 4, are thoriferous.

Monazite

Most of the thorium of commerce is obtained from the mineral monazite, which is frequently mined in placer deposits. Monazite is a cerium earth's phosphate which has been mined in Idaho, Florida and the Carolinas. These deposits are not rich enough to compete with those of Brazil, India and Ceylon. Formerly, much of the thorium nitrate produced was used in the manufacture of gas lamp mantles, but with the decline of their use the demand for thorium decreased.

Monazite is primarily an anhydrous phosphate of rare earths, such as cerium, lanthanum, and didymium, with small and varying amounts of thorium oxide, usually ranging from 3 to 9 per cent. Monazite is commonly an accessory constituent of gneissoid rocks, and is found widely distributed, but seldom in commercial amounts.

The simple test given by Ohly for identifying monazite is worthy of attention. A single grain of monazite is moistened with sulfuric acid on a microscope slide and warmed until the acid is driven off. The cerium will then crystallize out in double ball-shaped clusters of radiating needles, or minute isolated

crystals shaped like cucumber seeds. This crystallization is better shown by adding a drop of water and recrystallizing in a desiccator.

Monazite is an interesting mineral because of its helium content. Helium is evolved from monazite to the extent of 1 cc per g, at normal temperature and pressure, when the mineral is heated to 1000°C. This process is now being used as a source of helium.

Physical Properties

Metallic thorium is a soft, solid lead-like substance at ordinary temperatures. The metal is frequently obtained as a grayish, glistening powder which may be pressed together into a solid body. Thorium has an atomic weight of 232.12 and an atomic number of 90. Thorium consists of only one isotopic species of mass number 232. The specific gravity of thorium is about 11.75. The metal fuses at 1827°C, but it boils above 3500°C. The specific heat of thorium for the range 0–100°C has been found to be 0.027 cal. The resistivity of thorium is 18×10^6 ohm-cm. Unlike zirconium and titanium, it crystallizes in face-centered cubes.

Thorium prepared by the Marden process[93] is a coarse powder which is less active than uranium powder prepared by the same method. Coarse powders, however, are more resistant to spontaneous combustion, so the fine powders obtained during washing are discarded. When thorium powder stands in air for any length of time it soon becomes oxidized. When pressed into rods or buttons, it does not conduct electricity well, and consequently becomes difficult to sinter. The specific gravity of thorium prepared by this method is about 11.2, which is lower than that of fused or sintered metal.

To make thorium wire, according to Marden, the powder is pressed into a bar and heated by passing a current through it in vacuo. About 90 per cent of the current necessary to fuse the bar is usually used, but lower values also seem to give good

results. Although the melting point of the metal is high (1827°C), very pure metal powder can be sintered at temperatures as low as 800°C and good working wire obtained. When buttons are desired for X-ray targets or other uses, the thorium powder is pressed into the required shape and heated by induction in a vacuum furnace.

When thorium is free from impurities it can be made into fine wire. A bar ⅛ sq. in. can be worked down to wire 0.03 in. in diameter in the cold with no annealing and no difficulty from cracks or splits. Thorium wire can be drawn, but not immediately after heat-treating or annealing. The wire must be rolled or swaged to work-harden it before drawing, as the wire has low tensile strength in the annealed condition and is too soft for satisfactory drawing through dies. Iron or copper clad thorium can be worked down to very fine wire of almost any desired dimension. Thorium metal made by the Marden process is easily machined and shaped.

Thorium is subject to nuclear fission when bombarded with slow neutrons. This reaction is not so well known as the "splitting" of plutonium or the uranium 235 isotope. However, it may conceivably compete with uranium as a source of atomic power.

Unlike uranium, which is made up of three isotopes of masses 234, 235 and 238, usually present in the ratio of 17,000:139:1, thorium, having an odd atomic number, is made up of only one isotope, whose mass is 232. At present, the greatest obstacle to the utilization of energy from nuclear fission on a large scale is the impracticability of isolation of uranium 235 from the other isotopes. With thorium, whose isotopic constitution is homogeneous, the problem of isolation does not exist.

Chemical Properties

Metallic thorium is a stable solid at ordinary temperatures, being unaffected by water, even at 100°C. When thorium is heated in air, however, it burns with great brilliancy, forming

particles of the white oxide, thoria. When heated in a stream of chlorine, bromine or iodine, it forms the corresponding halide. The metal easily dissolves in nitric acid, more slowly in dilute sulfuric acid and hydrochloric acid. Aqueous solutions of alkalies do not affect thorium, but fusion with alkalies has a detrimental effect.

Compounds

Most thorium compounds are colorless and chemically resemble cerium in the higher state of oxidation. Most thorium salts are insoluble in water, except the nitrate, chloride, and sulfate. The principal form in which thorium is obtained is the oxide. Thorium dioxide (ThO_2), or thoria, is the only known oxide. It is inert toward most chemical agents. The molecular heat of formation of thorium oxide is higher than that of most other metallic oxides, i.e., 1385 kilojoule as against 910 for TiO_2 and 748 for ZrO_2. Thorium combines with carbon, nitrogen and boron. A silicide has also been prepared.

Extraction from Ores

The method used to extract thorium from its minerals depends upon the ore. Thorite is decomposed by heat and sulfuric acid, the sulfate extracted with water, and purified by reprecipitation from a hot solution. Monazite is treated with sulfuric acid, and oxalic acid is added to the filtrate to precipitate the thorium as the oxalate or double oxalate. Thorium is distinctive in that it readily forms soluble double oxalates when the oxalate reagent, e.g., ammonium oxalate, is added to soluble thorium salt solutions. Monazite may also be treated with sulfuric acid, and the solution obtained diluted slowly with an alkali. Thorium phosphate is precipitated and then converted into thoria by fusion with sodium carbonate.

Preparation of the Metal

There are several methods for preparing elemental thorium.

Thorium metal may be obtained by the action of sodium on the chloride, $ThCl_4$. Thorium chloride is produced by passing chlorine through a mixture of thoria and carbon. The double chloride of thorium and potassium can be heated with sodium to obtain the metal. The double fluoride of thorium and potassium may also be reduced with potassium.

A very satisfactory recent procedure for preparing pure thorium is that given by Marden.[93] Both uranium and thorium are prepared by similar methods. In the case of thorium, equal parts of potassium and sodium chloride are fused with potassium thorium fluoride and electrolyzed with a molybdenum cathode in a graphite crucible (the anode). The thorium metal powder adheres to the cathode. After removal from the bath and cooling, the deposit is washed with water, dilute acid, and then alcohol.

The bath temperature is approximately 775°C; cathode current density 90 ampere per sq cm, the current efficiency 60 per cent. The approximate bath composition is 500 g of KCl, 500 g of NaCl and 60 g of $KThF_5$.

Technology

Three principal uses have been found for thorium in recent years.[93] The photoelectric properties of thorium have made it useful for measuring restricted portions of the ultraviolet spectrum. In recent years, commercial X-ray tubes with thorium targets have been proposed. Recently, the consumption of thorium metal has been approximately 500 g per month for photoelectric cells and glow discharge tubes.

The work of Slack (quoted in Marden's paper [93]) compares the properties of thorium and uranium to those of tungsten, which gives an idea of their usefulness as X-ray targets. Some properties are listed in table 12. In research, thorium has been useful as a strong source of monochromatic X-rays. Two main difficulties have arisen, however, in its application. The melting point of thorium is lower than that of tungsten, therefore, with

fine focus and large energy input, it has a tendency to melt. If the metals are volatalized they may deposit on the cathode, subsequently affecting the electron emission and largely altering the operating characteristics of the tube.

Perhaps the best known application of thorium is in incandescent gas lamp mantles. This industry thrived in former years, but, of course, the introduction of the electric light, drastically reduced the manufacture of gas lamp mantles. They are usually composed of about 99 per cent thorium oxide and 1 per cent cerium oxide. Although the mantles have practically disappeared from the market, the commercial importance of thorium and mesothorium is even greater than before. Because of its high melting and sintering temperatures, thorium oxide is an ideal foundation for many catalysts, such as iron oxide, operating at very high temperatures.

Thorium finds some use as a "getter" in vacuum tubes. The substance can be employed in the colloidal state, mixed with the usual *getter*, facilitating final evacuation and maintenance of the vacuum in tubes.

Alloys

Thorium forms alloys with various metals, including tungsten and molybdenum. Many thousands of miles of ductile tungsten filament wire containing 0.75 per cent thorium are being produced. This thoriated tungsten filament is superior to ordinary tungsten filament, especially in electron-emitting qualities.

Among the alloys of thorium, those of Guertler [94] are of special interest because they are mechanically strong and chemically resistant. They contain 30 per cent Cu, 65 per cent Ni and 5 per cent Th; or 20 per cent Fe, 70 per cent Ni and 10 per cent Th; or 19 per cent Cr, 77 per cent Ni and 4 per cent Th. These alloys resist high temperatures and do not form a scale.

TABLE 12

RARER METAL X-RAY TARGETS

	Melting Point, °C	*Atomic Number*	*Density*	*X-Ray Efficiency*	*K Wave Length, Å*
Thorium	1845	90	11.2	120	0.134
Uranium	1690*	92	18.7	125	0.126
Tungsten	3370	74	19.3	91	0.208

* The pure uramium prepared in the manufacture of atomic explosives melts at 1150°C.

Radio-element Applications

The radioactive properties of thorium and other closely related radioactive elements find some use. Mesothorium is used medicinally in the treatment of cancer and skin diseases. It is employed as a substitute for radium in some instances, for example, in luminous pull-chain pendants, being much cheaper and about 30 times as powerful as radium.

Mesothorium is obtained from the residues of monazite sand after thorium and cerium have been extracted. The extraction process is similar to that used for the extraction of radium. The residues are treated with hot sulfuric acid, and barium salts are added to precipitate the mesothorium as a double compound with barium sulfate. This salt is filtered off, dissolved in sodium carbonate and purified by a long series of fractional crystallizations.

Radiothorium is another radioactive substance, which finds less use than mesothorium but is a stronger emitter of alpha rays than radium. Radiothorium is not used in clinical medicine, although, like mesothorium, it finds its way into the research laboratory. These substances can be used in highly specialized work. For example, they may be employed for testing minute leakages of air or dust through gas and dust masks and in the cloth used for their construction. Because of

their intense ionizing power they may find slight application for dissipating static electricity.

The dissipation of static electricity is extremely important in places where oil, explosives, and highly inflammable materials are being handled. Radium has been used for this purpose, but the cheaper thorium substitutes could supplant it. In a large Russian rubber factory radium is used to reduce fire hazard by preventing sparks from static electricity. When rubber flows upon a fabric base and dries on it, enormous charges of static electricity result from the friction of the rubber-covered fabric against parts of the drying machinery. These accumulated charges finally break down, or spark over, and a discharge becomes inevitable. The spark resulting constitutes a great hazard, especially when highly explosive vapors are present. The accumulation of charges is prevented by placing radium near the point where the static electricity is generated. The radioactive radiations ionize the air, making it a good conductor, so that dangerous charges flow harmlessly to the nearest metal part and finally to earth. The cost is very low, 1 mg of radium lasting indefinitely. The intense alpha-ray emission of thorium would make it an efficient discharge agent.[95]

Polonium is added to the electrodes of some spark plugs to ionize the air between the gap and facilitate passage of a hot spark under all temperature conditions.[96] The polonium is added to the spark plug alloy. It is reasonable to suppose that the thorium radioelements could be employed in the same capacity with superior results, as they are much cheaper and better ionizers because of the large amounts of alpha particles they emit. Alpha particles ionize 100 times as well as beta particles, and beta particles ionize 1000 times as well as gamma rays.

Luminous Pigments—Phosphors[97]

Small quantities of the thorium radioelements, notably of mesothorium, are added to self-luminous paints, which are so

valuable in instrument dials and for black-out applications. The mesothorium is added in very small amounts with a phosphor such as zinc sulfide, resulting in permanent luminosity.

For activating and exciting phosphors, especially those of the zinc sulfide type, a mixture of quinine, mesothorium, and thorium compounds may be used. This combination is important from several aspects. The quinine inhibits hydrolysis of the phosphor, which would generally take place in a moist atmosphere. The sulfide pigments are particularly susceptible to hydrolysis.

The radioactive mesothorium emits a radiation which continually excites light emission in the phosphor, and the thorium acts as the activator. Zinc sulfide (240 g) is treated with 5 g of quinine sulfate. This mixture is activated and excited with a solution of 0.25 mg of mesothorium bromide per cc in 10 cc of distilled water. A 10 per cent solution of thorium sulfocarbolate is added to the mixture, 9 cc of this solution being used. After evaporating to dryness, a self-excited phosphor is obtained. In handling mesothorium bromide the precautions taken for other dangerous radioelements are to be observed.

Analysis

Thorium is doubly important from the standpoint of the analyst. In addition to being detectable by ordinary chemical methods and reactions, thorium is radioactive. This means that the electroscope or other such device may be employed for the detection and determination of extremely small quantities of the element. As thorium is radioactive its presence in minerals, filaments and other materials may be indicated by its effect upon a photographic plate. However, several other elements, notably radium and uranium, have a similar effect, and therefore photographic and electroscopic procedures are not absolutely conclusive.

Ore Assay

In the quantitative determination of thorium in ore, a method that can be used is to heat 1 g of the finely divided mineral with hydrochloric acid until it is completely decomposed, about six or seven additions of acid being required before solution is insured. The whole is evaporated to dryness, the silica separated as usual, and hydrogen sulfide bubbled through the solution to saturation.

The precipitate formed is filtered off and the filtrate reduced in volume by evaporation. This solution is neutralized with ammonium hydroxide and the precipitate which forms, consisting primarily of hydrated thorium oxide, ferric hydroxide, and aluminum hydroxide, is filtered off and washed with water. The precipitate is then dissolved in sulfuric acid and this solution evaporated until a white voluminous mass separates out.

The white mass is neutral thorium sulfate, which is slightly soluble in water. The mother liquor is filtered off and the precipitate remaining on the filter washed with boiling water, dried, and ignited to thorium oxide. The filtrate is concentrated by evaporation and neutralized with potassium carbonate. A boiling, saturated solution of potassium sulfate is then added, from which potasium thorium sulfate crystallizes out. The solid is separated by filtration and washed with potassium sulfate solution. It is then dissolved in warm water and treated with ammonium hydroxide to precipitate the thorium as the hydrated oxide. This is washed, dried, ignited and weighed as thorium oxide. This weight is then added to the first weight obtained.[98]

Detection and Analysis

Cupferron may be employed to precipitate thorium quantitatively from acetic acid solution, although silver, lead, mercury, tin, bismuth, tungsten, and cerium interfere.[99] Similarly, picrolonic acid, 2.6 g/l, gives a precipitate of a thorium picro-

lonate which is less soluble than the calcium and lead picrolonates. The precipitation is obtained from acetic acid. The reagent cannot be employed to separate thorium from the rare earths, but in their absence it is satisfactory for the gravimetric determination of thorium.[100]

The Kaserer test [101] for zirconium employing the pyrogallolaldehyde reagent may be used for thorium. A bright yellow liquid forms with the reagent. Details are given in the section on zirconium analysis. Thorium salts are precipitated by a solution of 15 g of potassium iodate in 100 cc of water containing 50 cc of concentrated nitric acid.[102] Thorium gives a violet lake with alcoholic alizarin solution.

Comparison of seven methods for determining thorium shows that precipitation by potassium iodate is simplest and most accurate.

Phenyl arsonic acid gives a quantitative precipitation when added to thorium salt solutions in the presence of ammonium acetate and acetic acid.[103] Solutions of thorium, as well as lanthanum, cerium, and titanium, on being treated with ammonium hydroxide and 1 per cent pyrogallol solution, give colored precipitates which are not given by solutions of iron, chromium, cobalt, aluminum, manganese, and nickel. Ethylenediamine can be substituted for the ammonium hydroxide.[104] Sebacic acid precipitates thorium quantatively as thorium sebacate.

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CHAPTER IV

VANADIUM, COLUMBIUM AND TANTALUM

Introduction

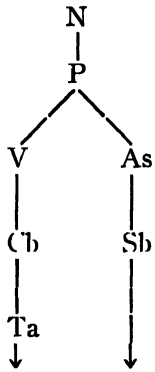
The three metals comprising the greater part of the vanadium family, i.e., vanadium, columbium, and tantalum, are all characterized by high melting and boiling points and by the difficulty of reducing their oxides to the metal. On the other hand, all 3 metals have a decided affinity for hydrogen. All are typical metals. They form many complex compounds. This is particularly true of vanadium, which is considered one of the most protean elements known. In fact, Saklatwalla [1] states that the chemistry of vanadium is as complex as the chemistry of carbon.

Of the three metals, columbium and tantalum are considered rare. Vanadium is more abundant in nature than copper, zinc, lead or tin. It makes up 0.032 per cent of the earth's 10-mile crust, according to Clarke and Washington. Columbium and tantalum are relatively unimportant biologically, but vanadium accumulates in natural deposits. The Colorado carnotite deposits are invariably associated with fossilized plant remains.

TABLE 13

PHYSICAL PROPERTIES OF THE VANADIUM-FAMILY METALS

Property	*Vanadium*	*Columbium*	*Tantalum*
Atomic weight	50.95	92.91	180.88
Atomic number	23	41	73
Atomic volume	9.3	13.3	23
Specific gravity	6.00	8.5	16.6
Melting point	1720°C	1950°C	3000°C
Boiling point	>3000°C	>3300°C	>4100°C
Usual color	Silvery	Silvery	Grayish



Arrangement of vanadium-family elements showing their relation to nitrogen and phosphorus

Vanadium

History

The discovery of vanadium is credited to Sefström, in 1830. He found the element in iron ores from Sweden during ordinary chemical analysis. Twenty-nine years previously, however, Humbolt and del Rio of Mexico announced the presence of a new element in plumbiferous ores from Zimapán, Mexico. These investigators called the new metal *erythronium*; later, however, they abandoned their discovery, believing the substance to be basic lead chromate.

After Sefström's discovery, Wöhler found that both new substances were identical, in fact, Wöhler himself had come very close to discovering the element in the same Mexican ore. He had set some of the ore aside for future investigation, but before he could get to it, Sefström's discovery was made known. At the time there was considerable competition among chemists in element discovering. Many chemists hunted for new metals and frequently bitter arguments would arise as to who had priority. Mellor [2] directs attention to the comment made by Berzelius at the time of the discovery of Wöhler:

"In the far north, there lived a goddess Vanadis, as beautiful as she was gracious. One day there came a knock at the door. The goddess was in no hurry and thought "they can knock again"; but there came no further knocking, for he who had knocked had passed on. The goddess wondered who it could be who cared so little to be let in and ran to the window, and recognized the departing one in the person of Wöhler. Some days afterwards someone else knocked repeatedly and loudly. The goddess opened the door herself to Sefström, and vanadium was discovered."

Berzelius worked out much of the basic chemistry of vanadium. However, during his investigations, Berzelius was under the impression that the oxide, VO, was the metal itself. By the year 1870, Roscoe had supplemented the work of Berzelius and practically exhausted the study from a chemical standpoint. Roscoe placed the element in its proper place with the phosphorus group and prepared the relatatively pure metal for the first time. He showed that the substance which Berzelius had thought to be pure vanadium was actually a mixture of vanadium nitride and vanadium dioxide, and that some of the compounds Berzelius had thought to be free from oxygen were really oxychlorides.

Mineralogy

Vanadium is never found in the native state, but some mineral species consist of relatively simple compounds, such as sulfides or oxides. Because of the superior qualities of vanadium steels, vanadium minerals are very important industrially. Vanadium minerals are not distributed widely, nor in large amounts, although there are concentrated in certain localities comparatively large quantities of vanadiferous ore.

When metallurgists began to become aware of the value of vanadium in steels, interest in the location and abundance of the ore began to increase. At this time, about 1905, Patron discovered the first large deposits rich in vanadium in the

Peruvian Andes, at an altitude of 16,000 feet. The mineral, an impure vanadium sulfide, has been named patronite after the discoverer.

Today the United States is the leading producer of vanadium ore with Peru running a close second. Third in importance is Africa (Rhodesia and S. W. Africa).

Types of Ore

Metallurgically, the ores of vanadium can be divided roughly into four classes according to their commercial importance:

I—Sulfides, such as patronite (Peru).

II—Silicates, such as roscoelites (Colorado).

III—Uranium-vanadium ores, such as carnotite (Colorado).

IV—Metallic vanadates, such as vanadinite, mottramite, and descloizite.

To extract the vanadium, each of these ores must be treated differently, and in most instances the final product is obtained by reduction at extremely high temperatures. The vanadium is tapped off from the crucible or furnace in the form of an iron alloy containing 30 to 35 per cent vanadium.

An important vanadium ore known as roscoelite, a complex silicate, is found in minute scales with a dark green to brownish-green color. Roscoelite has been found in Colorado and in parts of California. It is also found associated with carnotite and other minerals in the large deposits of the uranium mineral localities of Colorado and Utah.

Vanadinite, a complex lead chloride and lead vanadate, has been found in Arizona, New Mexico and several foreign countries. Vanadinite crystallizes in hexagonal prisms and has an uneven fracture. Its specific gravity is from 6.66 to 7.23. Another vanadium mineral known as descloizite is a lead vanadate containing iron, zinc, copper, and other substances as impurities. This mineral is found in Argentina in small olive-brown to blackish crystals having a bright luster. It has a Moh hardness of 3.5 and a specific gravity of 5.839. Descloizite is

found associated with other vanadiferous ores in New Mexico, Montana, and Arizona.

Endlichite, a variety of vanadinite, was analyzed by Ohly, in 1903, with the following results:

	Per Cent
V_2O_5	7.94
As_2O_5	10.73
P_2O_5	0
PbO	79.15
Cl	2.18

Endlichite differs from vanadinite in that it contains a larger amount of arsenic pentoxide, which supplants some of the vanadium pentoxide in vanadinite.

TABLE 14

VANADIUM MINERALS [3]

Mineral	*Per Cent Vanadium Pentoxide* *
Ardennite	0–9
Bismuth ocher	1–29
Brakebuschite	24–25
Calciovolborthite	37–39
Carnotite	19–20
Chileite	13–14
Cuprodescloizite	17–22
Dechenite	45–47
Descloizite	20–22
Mottromite	17–18
Patronite	18–19
Psittacinite	17–26
Pucherite	22–27
Roscoelite	21–29
Vanadic ocher	100
Vanadinite	8–21
Vanadiolite	44–45
Volborthite	14–15

* V_2O_5 contains 56.02 per cent V.

One of the most important vanadium-bearing minerals in the United States is carnotite. It has been mined for many years for its radium, uranium, and vanadium content. The characteristic color of carnotite is a canary yellow. It occurs in sandstones and in petrified wood throughout Colorado and Utah (see chapter 5). Carnotite was first described by Friedel and Cumenge in 1899. A typical carnotite from Montrose County, Colorado, contains 54 per cent uranium oxide and 18 per cent vanadium oxide.

There are not many mineral species containing vanadium as an essential constituent. Roscoelite is essentially a muscovite in which vanadium has partly replaced the aluminum. Roscoelite contains as much as 24 per cent vanadium oxide. Impure varieties containing a smaller percentage of vanadium have been mined in the sandstones of Colorado together with carnotite.

Vanadinite is found in the mining regions of Arizona and New Mexico, and often associated with wulfenite and descloizite. Brilliant, deep-red crystals have been found in a number of localities in Arizona, notably the Old Yuma mine near Tucson.

Physical Properties

Pure vanadium is a bright, silvery, ductile metal having a specific gravity of 6.0 at room temperature and a melting point of 1700°C.[4] At its melting point vanadium is one of the least volatile of metals; a sample may be held fused in a vacuum for a considerable time without showing appreciable evaporation, as evidenced by a blackening of the container walls.

The atomic weight of vanadium is 50.95 and its atomic number is 23. So far, physicists have found ordinary vanadium to consist of only one atomic species, that is, one isotope (of mass 51), in all minerals and compounds. Vanadium crystallizes in a body-centered cubic lattice, having a specific resistance of 26×10^{-6} ohm per mm.[5] The specific heat of vanadium

between 20 and 100°C is given as 0.120. The work function of vanadium is 3.79 electron volts.

It will be noted that few reliable values for the physical constants of vanadium are available. This is due to the difficulty of obtaining pure vanadium, and the presence of even small amounts of foreign metals will exert a considerable influence upon its physical properties. Therefore, many specialists on vanadium metallurgy consider some of the values given in the literature to be unreliable. All early attempts to produce pure vanadium failed. In 1927, however, Marden and Rich prepared very pure vanadium and checked the values for some of its physical properties. Their work shed new light on the true physical nature of vanadium.

Chemical Properties

Vanadium is one of the most interesting elements known. It rivals carbon in the large number and wide variety of complex compounds that it may form. Pure vanadium is very difficult to obtain, but it is stable in air and not affected by water at room temperature. The metal readily unites with nitrogen at red heat, forming a nitride. When finely divided and thrown into a flame, it burns brilliantly.

Vanadium is insoluble in hydrochloric acid and aqueous alkalis, but is readily attacked by hot sulfuric acid, aqua regia, and nitric acid. It is decomposed by fusion with sodium hydroxide, forming sodium vanadate, with the evolution of hydrogen. Vanadium metal, heated to 1300°C in hydrogen, reacts to form a hydride. The hydride has a decided embrittling effect on the metal.

Compounds

Vanadium compounds are known in five states of oxidation, as represented by the five oxides. The formation of bi, tri, tetra, penta, and hexavalent compounds complicates the chem-

istry of the element. Vanadium forms salts with many acids, and it also yields acids which form salts with bases.[1] The salts derived from the lowest oxide, VO, or V_2O_2, are powerful reducing agents, which bleach organic coloring matter and reduce to the metallic state compounds of copper, tin, silver, mercury, etc.

Vanadium compounds are characterized by their bright colors. Each oxide has its distinguishing color. For instance, the dioxide is brown or grayish, the trioxide is black, the tetroxide is blue and the pentoxide is red. The basic monoxide forms salts with chlorine which are violet. The trioxide or the corresponding hydroxide dissolves in acids to form green vanadic salts. The dioxide dissolves in bases to form black salts. It also forms oxy salts, known as vanadyl compounds, which are blue. The pentoxide can be converted into three vanadic acids, which form salts such as sodium metavanadate, $NaVO_3$, sodium pyrovanadate, $Na_4V_2O_7$, and sodium orthovanadate, Na_3VO_4. The orthovanadates and metavanadates are yellow.

Trivalent vanadium salts resemble ferric and chromic salts and form a long series of alums. The tendency to form double salts increases with the valency. Tetravalent vanadium oxide (vanadyl oxide or hypovanadic oxide), VO_2, is a very stable base, forming salts with most organic and inorganic acids. The vanadites, or hypovanadates, are readily oxidized to the vanadates. Pentavalent vanadium, as exemplified by vanadic oxide, V_2O_5 (similar to P_2O_5), is distinctly acid in character. This oxide forms a huge number of compounds and double salts. It can be obtained in a very pure state by igniting ammonium vanadate. Hexavalent vanadium is found in pervanadic acid, HVO_4, but little is known about its compounds.

Saklatwalla [1] points out that the difficulties of extraction of the metal and the large recovery losses were due to a lack of understanding of the complex vanadium chemistry.

A knowledge of the valences was necessary, for instance, in

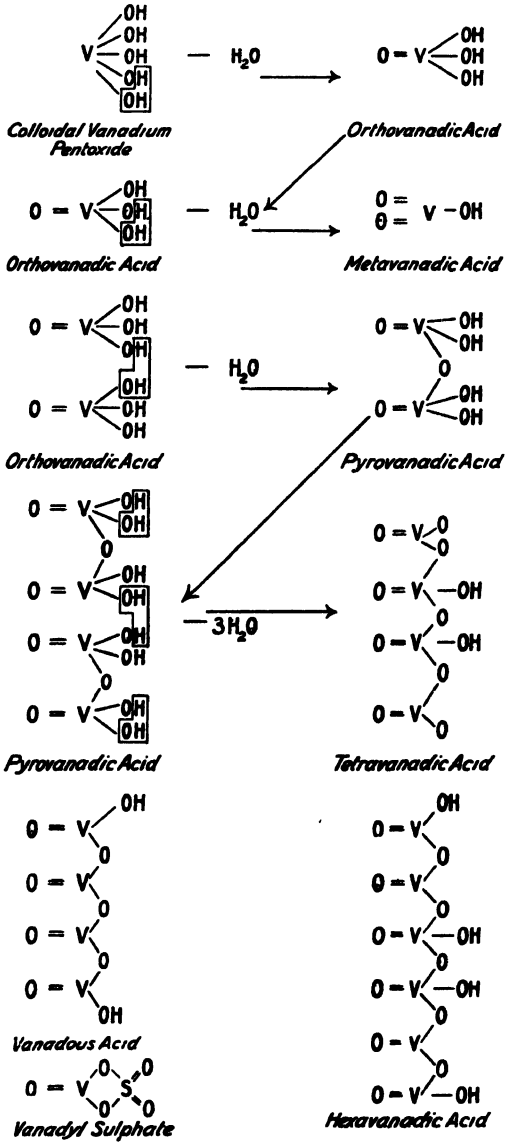


FIGURE 8
Scheme of vanadium chemistry

selecting a leaching agent for a mineral whose vanadium content is in a given state of valency, or in changing the valency to the value required for the leaching medium used. For selecting a reagent in precipitation, or the correct fluxes and refractory lining in reduction, the valency of vanadium had to be kept in mind.

Extraction from Ores

There are several methods for extracting vanadium oxide or vanadium metal from the ore. In each instance the efficiency of the method is a function of the quality of the ore, the chemicals and the equipment available.

In one laboratory method, the ore is fused with potassium nitrate, and the potassium vanadate formed is extracted with water. From the potassium vanadate, barium vanadate may be prepared by precipitation with a soluble barium salt. The vanadate is decomposed with sulfuric acid and the insoluble sulfate removed by filtration. The filtrate is saturated with ammonium chloride to form a precipitate of ammonium vanadate, from which vanadium pentoxide is obtained by ignition.

For the extraction of vanadium from carnotite, one method is to decompose the ore with nitric acid and treat the solution with sodium hydroxide and sodium carbonate. The vanadium remains as the insoluble sodium vanadate. The uranium and radium in solution are removed for further extraction.

In the extraction of vanadium from vanadinite, a similar procedure may be employed, although lead must first be precipitated as the sulfide from acid solution with hydrogen sulfide and filtered off before treating the solution with sodium hydroxide and sodium carbonate.

Several fusion processes have been developed. In one, the ore is fused with potassium bisulfate and the melt extracted with water. The extract is evaporated to a small volume and potassium uranyl vanadate acid sulfate crystallizes out. Van-

adium is reduced by zinc, precipitated as the ammonium compound, and ignited.

Wet-leaching processes have now been almost entirely replaced by the more efficient dry-smelting processes, which are based on the principle of matte smelting. In matte smelting, the ore (containing sulfur) is smelted in a reverberatory furnace, until all the heavy metals in the ore, such as iron, manganese, nickel, lead, copper, zinc, etc., are converted to a matte, leaving the vanadium in the slag, from which it is reduced to ferrovanadium alloy.

However, the inherent difficulties in these metallurgical processes render the extraction of vanadium both costly and wasteful. With improved methods of ore processing, it is possible to carry out the last stage of reduction to the metallic state without preliminary processing.

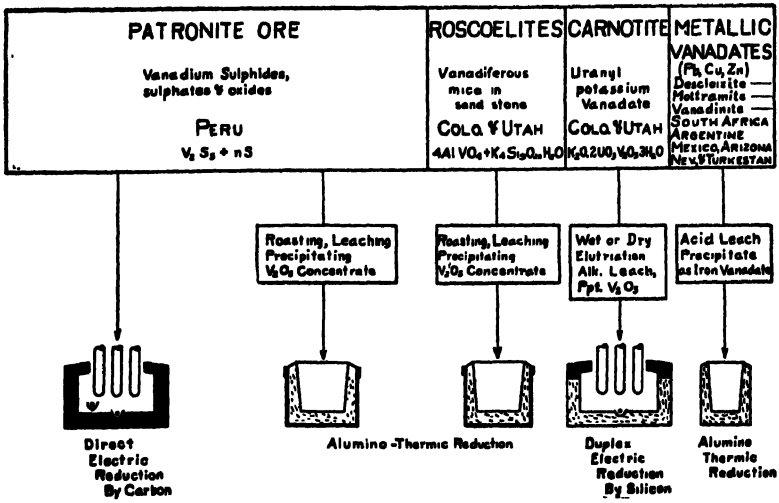


FIGURE 9

Vanadium ore processing schemes (reprinted from the Vancoram Review).

Electrothermic Reduction

The most significant advance in the large-scale extraction of vanadium from ores is the development of electro-thermic reduction and aluminothermic reduction.

In aluminothermic reduction, a mixture of aluminum grains and a metal oxide are raised to the reduction temperature. Instantaneous reaction occurs, the aluminum combining with the oxygen in the oxide to form a slag. The metal separates out below the slag. This method is used with a great deal of success on mixtures of iron oxide and vanadium oxide. The reduction of vanadium oxide alone, without iron oxide added, is too violent and impractical.

Aluminothermic reduction is not completely satisfactory, however. Carbon, silicon, manganese, silicon carbide, calcium carbide, boron, and boron carbide, have been tried as substitutes for aluminum. By the use of ferrosilicon and the upper flux, it is possible to extract ferrovanadium alloy by electrothermic reduction. In this process, the physical conditions of aluminothermic reduction are almost duplicated.

Laboratory Preparation of Vanadium Metal

A method for preparing pure, ductile vanadium is given by Marden and Rich.[4] The fundamental reaction is

$$V_2O_5 + 5Ca = 2V + 5CaO.$$

A charge consists of 175 g of V_2O_5, 300 g of $CaCl_2$ and 300 g of Ca powder or shavings. The charge is placed into an airtight, high-pressure steel reaction vessel and heated to 950°C for 1 hour. The steel bomb is then allowed to cool and the vanadium metal pellets separated from the calcium chloride and calcium oxide by washing with cold water. The pellets are melted under vacuum into a small ingot. The metal, 99.3 to 100 per cent pure, is extremely ductile.

According to van Arkel[6] a better method is the thermal

decomposition of VI_2 on an electrically heated vanadium wire mounted in a quartz bulb.

Technology

Ferrous Metallurgy

The most significant application of vanadium is in metallurgy, particularly in ferrous metallurgy. When added to steel, vanadium scatters the impurities and gives it a fine grain. Vanadium can be added to air-cooled steels and to those which are heat treated. It yields a homogeneous product in large forgings and castings.

The addition of 0.2 per cent vanadium to cast iron improves its macrostructure and microstructure. It affects the size, form,

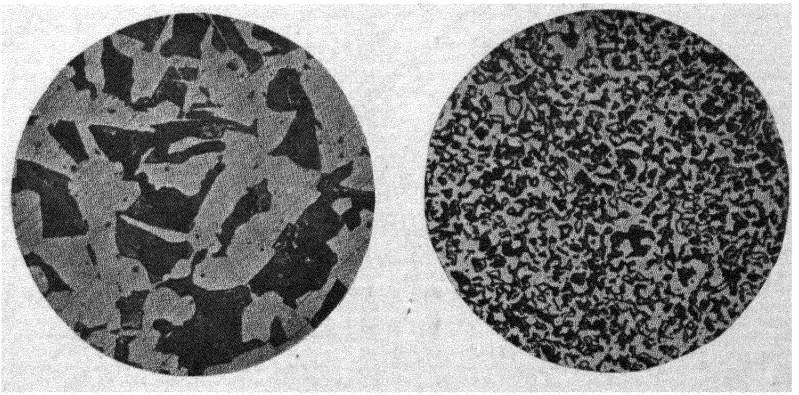


FIGURE 10

Effect of vanadium on grain size of steel.

Right, ordinary carbon steel; left, steel with 0.2 per cent vanadium; magnified 100X.

and arrangement of the graphite particles, which determine many of the physical properties of the alloy. The addition of vanadium to cast iron increases the tensile strength and hard-

ness. Resistance to impact, machinability, ductility, transverse strength, and compressive strength are all increased by the presence of vanadium.[7]

Manganese–vanadium steel possesses high strength and ductility. It may be more conveniently worked and with less harm to physical properties than many other steels. This new steel is used for making rivets of greater structural strength. The metal is most important, however, for plates, ships, and flats in which the steel is manufactured by either open-hearth or electric-furnace methods. Its chemical composition must conform to the following:

	Per Cent
Carbon	0.18 maximum
Manganese	1.45 maximum
Silicon	0.15 to 0.30
Phosphorus	0.04 maximum
Sulfur	0.05 maximum
Vanadium	0.08 to 0.12

Vanadium steel castings have been employed extensively in locomotives, drag equipment, trucks, buses, and other heavy-duty machinery. It is valuable in transportation units and other mobile equipment because of its resistance to impact and fatigue. Carbon-vanadium steel castings are of relatively simple composition:[7]

	Per Cent
Vanadium	0.15 minimum
Carbon	0.30 to 0.38
Manganese	0.75 to 1.00
Silicon	0.25 to 0.50
Phosphorus	0.05 maximum
Sulfur	0.05 maximum

Metallurgists have worked out new iron and vanadium alloys which include other elements, such as chromium, manganese, nickel, etc. For example, a series of process alloys has been developed.[8] These complex alloys, called Grainal, produce very unusual results when added to steel, usually in a concentration of from 2 to 5 lb per ton of steel. The composition of Grainal may be represented by the formula, FeVTiAl.[9]

One of its applications is for increasing the hardenability of steel. Even in fine-grained steels, which have been shown to be rather shallow-hardening, deep-hardening may be secured by the addition of Grainal. Certain carbon steels, which ordinarily can be fully hardened only in water, have been changed by the addition of Grainal into steels completely hardenable by oil.

Grainal also contributes to quenched and tempered steels of high hardness, tensile ductility and impact strength. It is used for making steel articles that are subject to surface-hardening treatments, such as carburizing, cyaniding, nitriding, quenching heated surfaces, etc.

Non-ferrous Metallurgy

The uses of vanadium in metals other than iron are not extensive. A few investigators have employed vanadium in bronze as a substitute for manganese to increase tensile strength, elongation, and area reduction.

Vanadium-bronze is used in the aircraft industry for propellor bushings, to give high strength and corrosion resistance. However, vanadium-copper alloys are of greater importance in this field. Vanadium-copper is also suited for making submarine and ship parts which must withstand the corroding effects of salt water.

Vanadium-aluminum alloys have greater stiffness than many other aluminum alloys used for making airplane frames. An alloy of aluminum and 53 per cent vanadium has been de-

veloped, which is very hard and has superior resistance to acids.

Vanadium finds some application in precious-metal alloys for jewelry and dental work. Vanadium hardens gold and may be used for coins and dental bridges.

Vanadium as a Catalyst

Alexander has given a good discussion of the properties of vanadium as a catalyst.[10] As far back as 1892, Walter [11] used vanadium peroxide to catalyze the oxidation of toluene to benzaldehyde and benzoic acid, and of anthracene to anthraquinone. It is also used to oxidize alcohol to acetaldehyde and acetic acid, diphenylamine to carbazole, and benzene to diphenyl.

Several patents have been granted for the use of vanadium as a catalyst for the electrolytic oxidation or reduction of organic compounds. In sulfuric acid manufacture, vanadium is superior to platinum as the catalyst because of its lower cost. It has also been shown that vanadium is not poisoned by arsenic and other substances, and therefore, it can be used under conditions in which platinum would not be satisfactory. Nickell [12] has pointed out that vanadium catalysts may replace platinum catalysts completely for sulfuric acid manufacture.

Medical and Biological Applications

The relationship of vanadium to the metabolism of some living organisms has been discussed in several papers.[13] Vanadium salts are poisonous when taken in large amounts, causing vasoconstriction, mainly in the splanchnic area, and exerting an inhibitory effect upon the respiratory center. When vanadium salts are ingested they cause gastrointestinal irritation. Continued ingestion may cause the destruction of kidney tissue.

Vanadium compounds are infrequently prescribed, although they have been listed in the *Materia Medica*. There is disagreement on the effectiveness of vanadium compounds as germicides.

Organo-vanadium compounds have recently been introduced as specifics for the treatment of diseases, such as syphilis. When given intravenously as the sodium orthovanadate, together with mercury inunction, they cause symptomatic relief and the disappearance of the Wassermann reaction, according to Freund.

Vanadium has been proposed as a hematinic for malnutrition and anemia. Investigators report that improved appetite, and a gain in weight and general vigor resulted from its use. Temporary benefits were observed when vanadium was given for diabetes mellitus.

Vanadium has found some use in topical therapeutics as an antiseptic and a skin stimulant. It has also been applied to the mucosa of the bladder, vagina, and uterine canal. Very dilute solutions are used, the concentration of vanadic acid ranging between 0.05 and 0.17 g/l.

A solution of vanadium oxychloride, 1:1000, in saturated sodium chlorate solution has been used for the treatment of ulcers, superficial abscesses and infected wounds with questionable success. Surgical powder made from the usual constituents (bismuth subgallate and sodium perborate) and small amounts of vanadium compounds may replace iodoform and some of the more expensive dressing agents.

Vanadium compounds have been given internally for chronic rheumatism, rheumatoid arthritis, neurasthenia, and similar conditions. The use of vanadium compounds is based upon their possible value as oxidizers and general stimulants for the digestive and metabolic processes. They are a means of supplying oxygen. Thus, in anemia, they compensate somewhat for the deficiency of hemoglobin in the system.[13] They are also believed to assist the defense mechanisms of the organism in acute infections, particularly influenza and pneumonia.

Other Uses

In view of the toxicity of vanadium compounds, they may possibly be used as fungicidal and insecticidal agents. The soluble vanadium salts would be most suitable, but the use of

vanadium pentoxide is also possible. It is likely that complex double salts of copper, arsenic and vanadium have a lethal effect upon many insect and fungus pests.

Vanadium compounds, with their wide variety of colors, have already gained some importance in the paint and pigment fields. Vanadium oxide acts also as a drier for linseed oil, being about twice as effective as manganese driers and about five times as effective as lead driers.

De Ment has prepared a vanadium stearate by the following reaction:

$$VCl_2 + 2NaC_{18}H_{35}O_2 = V(C_{18}H_{35}O_2)_2 + 2NaCl.$$

The method is the same as that used for the production of other metallic soaps. The product of this reaction is a deep blue-gray solid which consists of vanadium stearate and several other salts of vanadium. Vanadium stearate is a useful, low-priced organo-vanadium compound for fungicidal paints.

It has been demonstrated by De Ment that many organo-vanadium compounds are brightly fluorescent under ultraviolet light, suggesting their application in fluorescent paints.

Vanadium inks are more permanent and less corroding to fountain pens than ordinary inks. The first vanadium ink was discovered by Berzelius.[14] It was prepared by adding ammonium vanadate to a filtered extract of galls. A few drops of vanadate solution changes a large volume of gall extract to a deep-black fluid.

Vanadium also exerts a catalytic effect on aniline dyes. One such dye preparation consists of the following:[15]

Aniline chloride	8	lb
Potassium chlorate	4	lb
Water	10	gal
Hydrochloric acid	0.5	lb
Ammonium vanadate	70	grains

Another vanadium ink can be made by adding neutral ammonium vanadate to hydrogallic acid in a gum arabic vehicle.[16] This ink is indelible and permanent, but after long periods of time it turns a slight greenish gray.

There are many minor applications of vanadium. It is used in making an aniline printing ink. A mixture of aniline hydrochloride and a source of oxygen, such as a chlorate, is treated with a vanadium catalyst. In current practice, 1.2 mg/l of vanadium are used for preparing a printing ink containing about 80 g of aniline hydrochloride. This corresponds to the extremely low concentration of 1 part vanadium in more than 66,000 parts aniline salt. The amount of vanadium employed varies inversely with the aniline content, temperature, and time of oxidation.

In photography vanadium salts are used for toning silver prints, and mixtures of uranium and vanadium are used for printing. Vanadium pentoxide in sulfuric acid and water is a developer. Its superiority lies in the fact that it can be used over and over again, being regenerated by merely adding zinc.

Vanadium finds application in special filter glass for eliminating short wavelength ultraviolet light. It also reduces photochemical action when present in the nitrocellulose of safety glass. Vanadium salts could be added to gasoline and petroleum products to prevent deterioration and gumming from exposure to sunlight.[17]

Analysis

In the gravimetric analysis of vanadium, the pentoxide is usually weighed and the metal content calculated from it. The pentoxide may be obtained by precipitating lead or barium vanadate, treating it with sulfuric acid, filtering, evaporating the filtrate, and igniting the residue. Vanadium pentoxide may also be prepared for gravimetric estimation by precipitating and then igniting mercury vanadate. It is also possible to precipitate

comparatively unstable ammonium vanadate, and on ignition obtain the pentoxide.[3]

Volumetric Analysis

In the volumetric analysis of vanadium, several methods may be employed. It is possible to reduce the vanadium compound by boiling with hydrochloric acid or an alkali halide in acid solution, and then titrate the liberated halide. The reduction may also be accomplished by boiling the solution containing vanadium with an organic acid such as citric, oxalic, or tartaric acid. The compound is titrated with standard iodine solution.

Vanadium produces blue colorations when its solutions are added to gallic, pyrogallic, or tannic acid.[18] To test for the presence of vanadium in water, a reagent is prepared by adding 0.2 g of diphenylamine to 100 cc of distilled water, warming on a water bath, cooling and filtering. This reagent (1 cc) is shaken up with 1 cc of concentrated hydrochloric acid and 1 or 2 cc of the water to be tested. If vanadium is present, a violet coloration appears, the intensity and rate of color development indicating the quantity of vanadium present in the water.[19]

Hydrogen peroxide is a reagent for vanadium, as well as for molybdenum and cerium. A 30 per cent solution of hydrogen peroxide forms a brown coloration in the presence of vanadium in sulfuric acid. A yellowish-green color, which is removed by boric acid, is given under the same conditions by molybdenum. Neutral solutions of cerium salts give an orange or yellow color on addition of 30 per cent hydrogen peroxide and quinine hydrochloride.[20]

Microchemical Tests

Martini [21] has proposed several microchemical tests for vanadium. To a drop of dilute vanadium salt solution, a drop of a saturated solution of hexamethylenetetramine sulfate is added,

mixed, and a drop of a saturated solution of ammonium thiocyanate introduced. A bright red precipitate forms. In another test, to a drop of a 1 per cent vanadium salt, a small amount of saturated pyrocatechol acetate solution is added until an orange color forms, and then a small amount of aniline is added. Black crystals form. Finally, to a drop of a 1 per cent vanadium solution, pyrocatechol is added until an orange coloration develops, then a drop of benzylamine and a drop of acetic acid are mixed into it quickly. Groups of orange crystals form.

In a solution containing 20 per cent nitric acid, 5,7-dibromo-8-hydroxy quinoline reacts with iron and vanadium to form green and brown precipitates, respectively. The test may be employed to detect trivalent vanadium in the presence of ferric ions by first adding an excess of sodium hydroxide to precipitate the iron as the hydroxide.[22]

When triethanolamine is added to a boiling, acidic solution of a vanadate, the solution becomes green, then changes to a brilliant blue.[23] Krech's test for vanadium in ores consists of passing chlorine through a sample mixed with excess wood charcoal, at a temperature of from 300 to 400°C. The volatile vanadyl chloride is hydrolyzed by treating it with sulfuric acid. A bright orange coloration (vanadium pentoxide) indicates the presence of vanadium.[24]

To test for vanadium in metals, especially steel, steel turnings are dissolved in dilute nitric acid, ammonium persulfate is added, and the solution heated until gas evolution has subsided. After cooling, the mixture is decolorized with phosphoric acid. When hydrogen peroxide is cautiously floated on the mixture, a red-brown zone appears, indicating vanadium. As little as 0.01 per cent of the element may be detected by this test.[25]

Another test for vanadium is to oxidize the solution with concentrated nitric acid and place a drop on a filter paper moistened with aniline hydrochloride. A greenish-blue ring

forms if vanadium is present. If the solution contains a chromate, chlorate, permanganate, or hypochlorite, it must first be boiled with concentrated hydrochloric acid.[26]

A simple, although not too positive, test for vanadium is the formation of a reddish-brown to red coloration when hydrogen peroxide is added to an acidic vanadium solution. An excess of hydrogen peroxide is to be avoided. A modification of this test is to treat the solution, containing 15 to 20 per cent sulfuric acid, with 1 drop of hydrogen peroxide and noting the color after 1 minute.[27]

In the Ephraim test, to 1 cc of concentrated hydrochloric acid, 1 cc of the test solution is added and evaporated rapidly to a volume of 0.4 cc in a test tube. It is then cooled in water, 1 drop of freshly prepared 0.1 per cent ferric chloride solution and 2 drops of 1 per cent dimethylglyoxime solution are added and made alkaline with ammonium hydroxide. The presence of vanadium is indicated by the formation of a red color.[28]

Columbium

History

The discovery of columbium (frequently called *niobium* in Europe) was made in 1801 by the English chemist Hatchett. Hatchett was investigating a specimen of heavy, black stone having golden streaks of mica, which he had obtained from the United States. He found that it contained 75 per cent of an unknown metal, which differed considerably from all the known metals. Hatchett named it *columbium* in honor of the country from which the ore came.

But in 1844 the chemist Rose announced the discovery of a new element which he called *niobium*. It was very similar to tantalum, which had been discovered a year after Hatchett's investigations.

Some controversy ensued, a few investigators holding that columbium, niobium, and tantalum were identical, and others believing that columbium and niobium were the same, but

tantalum a different, though closely related, element. It was later shown that columbium and niobium were identical, and that tantalum was a different element.

Hatchett was given credit for discovering the element and *columbium* became the accepted name in most countries except Canada, England and Germany, which long retained the term *niobium*. It was not until a few years ago that the name *niobium* began to disappear from chemical literature. At the present time *columbium* is the accepted name for the element.

Mineralogy

There are 3 general types of radioactive ores.[29] Type I includes the uraninites and other pure uranium compounds. Type II consists of the alteration products of Type I minerals, e.g., torbernite, and other minerals, such as carnotite, the most important representative of this class. Type III includes many of the columbium titanium-tantalates.

Dana[30] has classified the minerals of columbium and tantalum. Columbates and tantalates are chiefly salts of metacolumbic and metatantalic acid. There are five groups of columbates and tantalates:

I. Pyrochlore Group. Isometric minerals, including pyrochlore, a complex of columbium, titanium, thorium, oxygen and other elements; koppite, a complex of columbium, oxygen, sodium, fluorine and other elements; hatchettolite, containing tantalum, columbium, some uranium and others; and microlite, primarily a calcium metatantalate.

II. Fergusonite Group. Tetragonal minerals, including sipylite, essentially an erbium columbate and fergusonite (a complex of columbium, tantalum, cerium, and other rare elements).

III. Columbite Group. Mainly orthorhombic minerals, represented by columbite, a complex of iron, manganese, and columbium; tantalite, whose composition is analagous to that of columbite; skogbolite, an iron metatantalate; and tapiolite, a tetragonal mineral consisting of iron tantalo-columbate.

IV. Samarskite Group. Orthorhombic complex columbo-

tantalates containing rare earths and other metals, represented by yttrotantalite, samarskite, annerodite, and hielmite.

V. Eschynite Group. Orthorhombic minerals usually containing titanium in addition to the elements in group IV, represented by eschynite, polymignite, euxenite, and polycrase.

TABLE 15

COLUMBIUM AND TANTALUM MINERALS[a]

Mineral	*Per Cent Columbium Pentoxide* *	*Per Cent Tantalum Pentoxide* †
Adelpholite	41-42‡	
Blomstrandite	49–50‡	
Cassiterite		0– 9
Columbite	26–77	1–77
Eschynite	32–33	21–22
Euxenite	18–35	
Fergusonite	14–46	4–43
Hatchettolite	63–67‡	
Hielmite	4–16	55–72
Koppite	61-62	
Loranskite		47
Marignacite	55-56	5– 6
Microlite	7– 8	68–69
Neotantalite	23	60–61
Polycrase	19-25	0– 4
Pyrochlore	47–58	
Samarskite	41–56	14–27
Stibiotantalite	7.5	51
Tantalite	3–40	42–84
Tapiolite	11–12	73–74
Wohlerite	12–14	
Yttrotantalite	12–13	46–47

* Cb_2O_5 contains 69.99 per cent Cb.
† Ta_2O_5 contains 81.93 per cent Ta.
‡ $Cb_2O_5 + Ta_2O_5$.

A great many columbium and tantalum minerals have been described [31] in the literature, and there is evidence of duplication, since identification was performed with restricted amounts of specimen. One of the main sources of columbium is the

mineral columbite, which may be found in alluvial deposits usually as small grains.

Columbite

Columbite, $(Fe,Mn)(Cb,Ta)_2O_6$, is the columbate and tantalate of iron and manganese. If the tantalum content is greater than the columbium content, the mineral is called tantalite. The iron and manganese contents also vary widely. Tin and tungsten may be present in small amounts.

When the iron is largely replaced by manganese, the mineral is called manganocolumbite or manganotantalite. The four minerals just described and minerals of intermediate composition are all found together in many deposits.

Columbite is found in the Pike's Peak region in Colorado, associated with microcline and complex silicate minerals resembling feldspar. It also occurs as crystals in the Black Hills of South Dakota together with beryl, cassiterite, and spodumene. Frequently huge masses of columbite have been found weighing more than 2 tons. The eastern and southern states yield some columbite.

The mineral is usually iron black, and some varieties are gray or brownish. They are all opaque. There is also a rare form of columbite which is translucent and reddish-brown in color. Most specimens of columbite exhibit submetallic luster and iridescence, and all streak from dark reddish to black. Columbite varieties are generally brittle, having a hardness of about 6 and a specific gravity of between 5.3 and 6.

Other Columbium Minerals

Hatchettolite and fergusonite are other important columbium minerals. Hatchettolite is mainly uranium columbotantalate and is important because of the two other rare elements which it contains. Hatchettolite is found in Mitchell County, North Carolina. It is a yellowish-brown, brittle, translucent mineral

of conchoidal fracture. It has a hardness of 5 and a specific gravity of between 4.7 and 4.9.

Fergusonite is essentially a metacolumbate and a tantalate of yttrium, containing erbium, cerium, uranium, and other elements in small amounts. It is found in the pegmatite dikes of the New England States, in Mitchell County, North Carolina, and in Llaono County, Texas. The Barringer Hill locality of Texas has large masses and even rough crystals of fergusonite; it is one of the few localities in the United States where fergusonite has been mined on a commercial scale. The columbium and tantalum minerals are frequently found associated with granitic rocks, like the coarse pegmatites.

Physical Properties

Pure columbium is a steel-gray, lustrous metal.[32] It is malleable, ductile, and about as hard as wrought iron. The specific gravity of columbium is 8.5 at 20°C and its melting point is 2150°C, at which temperature it ignites when in a finely divided state. Columbium boils at temperatures above 3300°C. The atomic weight of columbium is 92.91 and its atomic number is 41. The element is made up of only 1 isotope, whose mass number is 93.

Chemical Properties

Columbium metal is resistant to the action of most chemical reagents. It is not affected by hydrochloric acid, nitric acid, or aqua regia. Concentrated sulfuric acid readily converts it into the hydroxide. Columbium has four different valences. Three oxides, the mono-, bi-, and pentoxides, are known, and a trichloride exists. Columbium is weakly basic. Its principal compound is the columbate, but it also combines with hydrogen and nitrogen. It is attacked by fused alkalis and by chlorine at red heat.

Compounds

The compounds of columbium are very much like those of tantalum, since they are closely associated in most of their minerals. The lower columbium oxides are dark powders and the pentoxide is white. The dioxide is soluble in hydrochloric acid and the pentoxide dissolves in sulfuric acid with difficulty, ignition decreasing its solubility.

Ammonium chloride precipitates columbic acid from solutions of columbium salts, especially when alkaline carbonates are present. Columbium forms a large number and wide variety of compounds. Probably the most important complex columbium salt is potassium fluoxycolumbate, which is used for the separation of columbium from tantalum by fractional precipitation.

Extraction from Ores

Columbium and tantalum are extracted simultaneously from ores, such as columbite and tantalite, in which they occur together. The procedure is to fuse the finely divided mineral with about 7 parts potassium bisulfate and extract the melt with hot dilute hydrochloric acid solution. A residue remains which is treated with ammonium sulfide to remove tin, tungsten, etc., and again extracted with dilute hydrochloric acid.

After this treatment the residue is washed well with hot distilled water and dissolved in hydrofluoric acid. The solution is filtered and potassium carbonate added to the filtrate. The double potassium-tantalum fluoride first begins to separate out, after which the double columbium salt crystallizes in plates.

A similar method for extracting these elements from their ores is to mix intimately 3 parts of acid potassium fluoride with 1 part by weight of the finely ground mineral and fuse thoroughly. The melt is extracted with hot hydrochloric acid solution, evaporated to a relatively small volume, and allowed to stand. The tantalum salt separates out first, followed by the

columbium salt. Purification is achieved by fractional crystallization.

An entirely different extraction procedure is that recommended by Fink and Jenness.[33] Common leaching agents have no effect on these refractory columbium-tantalum ores, but Fink and Jenness discovered that a leaching solution containing both hydrofluoric and oxalic acid is very effective. The columbium and tantalum in the leach liquor are subsequently precipitated out by adding ammonia while keeping the solution acid to litmus.

Preparation of the Metal

Columbium can be prepared by aluminothermic reduction or by reduction of the oxide with carbon in vacuo.[32] Mischmetal, an alloy containing rare earth metals, has also been used for the production of the metal. (See tantalum section following.)

A reliable method of preparing metallic columbium is an electrochemical one. Columbium oxide is converted to the fluoride, which is introduced into a molten bath of potassium fluoride. The columbium metal powder precipitated on the cathode is carefully washed and dried. It is then pressed into rods and sintered in vacuo.

Technology

Columbium is one of the trace elements that plays a very important role in metallurgy. For a number of years it had been known that stainless steel (18 per cent Ni, 8 per cent Cr) was susceptible to "intergranular corrosion" at elevated temperatures. The hard plates of stainless steel would become "mushy," due to lack of cohesion between the metal crystals. Becket [34] ascertained the cause and cure of this intergranular corrosion in the 18/8 steels. He discovered that the addition of a small percentage of columbium (about 1.0 per cent) to the steel was "the most satisfactory solution of the intergranular corrosion problem." Columbium acts as an inhibitor. The carbon in the

steel combines with the columbium, thus preventing segregation on the grain boundaries. Today, therefore, the 18/8 steel may be used at high temperatures, such as are attained during welding.

The columbium ore used by Becket was imported from Nigeria, where it occurs associated with cassiterite (SnO_2).

Ferrocolumbium

The ore from Nigeria is concentrated and the columbium alloyed with iron to form ferrocolumbium. The reduction by silicon is carried out in electric furnaces at Niagara Falls. The columbium is added to the 18/8 steel as ferrocolumbium. The consumption of columbium for this purpose is approximately 150 tons per year.

Other Alloys of Columbium

Columbium alloys with cobalt, nickel and chromium. Very little is known about the non-ferrous columbium alloys.

Analysis

The determination of columbium (and tantalum) in ferrocolumbium is a very lengthy procedure, details of which are obtainable.[35]

Tantalum

History

At the time of Hatchett's discovery of columbium, the Swedish chemist Ekeberg was studying two new minerals, one from Kimito, Finland, and the other from Ytterby, Sweden. He named these minerals tantalite and yttrotantalite, respectively, and upon analyzing them, found a new metal. He chose the name tantalum for the element because of the "tantalizing" difficulties he encountered trying to dissolve the minerals in acids.[36]

Mineralogy

The mineralogy of tantalum is very similar to that of columbium. In fact, it is often difficult to distinguish between the two elements by ordinary tests.

Tantalite

The important mineral tantalite, a tantalate of iron and manganese, is found in Sweden, Finland, France, the United States, etc. The mineral is never found in large amounts. Tantalite is opaque, brown to black in color and has a metallic luster. The hardness varies from 6 to 6.5.

Tantalite, like columbite, is often found in the form of small grains or masses, embedded in granitic rocks of the pegmatite variety. Much of the columbium and tantalum of commerce is recovered as a by-product from alluvial deposits. For example, the cassiterite-bearing sands of northern Nigeria, Africa, contain relatively large amounts of columbite and tantalite, along with the cassiterite. The various minerals are separated by magnetic means, the cassiterite content is concentrated to about 65 per cent and sacked for shipment to England for refining. For many years the columbite and tantalite in the Nigerian deposits were dumped into huge pits as waste material. Later, when a wider demand came for columbium and tantalum, this former waste material was recovered and sold at a premium over cassiterite.[37]

Physical Properties

Tantalum is a silvery metal which melts at 2996°C and boils above 4100°C. The specific heat of tantalum is 6.5 at 20°C. It has a thermal expansion coefficient of 7×10^{-6} at 20°C. The electrical resistivity of tantalum is 15×10^{-6} ohm-cm at 20°C. The metal was once employed for filaments in incandescent lamps. Tantalum is hard, very ductile and malleable, being easily rollled into sheets. Its specific gravity is 16.6.

The atomic weight of tantalum is 180.88 and its atomic number is 73. Like columbium, tantalum is made up of only one isotope of mass number 181.

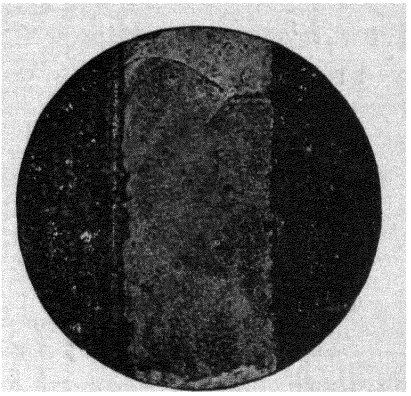


FIGURE 11

Micrograph of ductile tantalum wire, magnified 100X (courtesy of Westinghouse Research Laboratories).

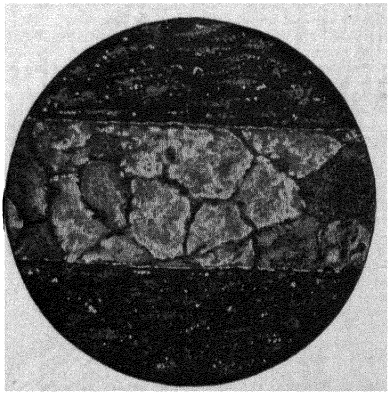


FIGURE 12

Micrograph of brittle tantalum wire, magnified 100X, showing tantalum hydride impurity in grain boundaries (courtesy of Westinghouse Research Laboratories).

Chemical Properties

Pure tantalum is not affected appreciably when exposed to air or water at ordinary temperatures. It is not dissolved by any acid except a mixture of hydrofluoric and oxalic acids. It resists the action of aqua regia. However, it may be dissolved by fused alkalis or by a mixture of nitric and hydrofluoric acids. The chemical properties of tantalum are very much like those of columbium, as has been mentioned previously. Under the proper conditions the finely divided metal will burn in air to the pentoxide.

Compounds

The usual valence of tantalum is 5, as in the white pentoxide, Ta_2O_5. Tantalum also exhibits tetravalency, as illustrated by the tetroxide, which is a very hard, dark-gray to whitish solid, not affected by acids. When tantalum tetroxide, Ta_2O_4 or TaO_2, is heated in air or oxygen it is converted to the pentoxide, which is more soluble in acids.

Other compounds of tantalum, particularly the halides, resemble in general the corresponding columbium analogs. However, when double salts are formed, differences in physical characteristics become more apparent and it is on this basis that the two elements can be separated or distinguished in complex mixtures.

Tantalum, at low red heat, combines with many elements to form carbides, nitrides, hydrides, etc. Some of these compounds may be used for alloying. It is more expedient to introduce tantalum as the carbide in alloys with other metals, such as iron. Solution of the metal and alloying takes place at lower temperatures than would be necessary if pure tantalum were employed. This principle is followed in many metallurgical operations on other metals which are refractory in the pure condition.

Tantalum is precipitated from its solution by hydrochloric acid as the pentoxide, but the compound later dissolves in its

mother liquor. The hydroxide is precipitated from hydrochloric acid solution by ammonium sulfide. The addition of tartaric acid inhibits precipitation. Ammonium sulfate and ammonium chloride also cause the same reaction to take place.

Metallic zinc in hydrochloric acid does not reduce tantalum pentoxide. When potassium ferrocyanide is added to acidic tantalum solutions, a yellow to white precipitation occurs. When ammonium hydroxide is added, this precipitate immediately turns brown. It dissolves in an excess of ammonium hydroxide.

Preparation of the Metal

The preparation of pure tantalum by fused salt electrolysis is similar to the method given for columbium. It is possible to obtain pure tantalum from potassium fluotantalate by reducing it with potassium metal and extracting the potassium fluoride with water. Other means of reducing tantalum compounds, particularly the double salts, have been employed. Mischmetal has been used on the oxide. A recent development is the reduction of fused $NaTaCl_6$ by metallic calcium.

Technology of Columbium and Tantalum

Tantalum has a higher melting point than all other metals except tungsten and rhenium. The melting point of columbium is higher than that of chromium. Both tantalum and columbium are readily soluble in molten ferrous metals at normal melting temperatures. Little work has been done on the non-ferrous alloys of the two metals, but the ferrous metallurgy has become fairly well developed.

A tantalum-tungsten alloy has been made commercially for special radio valve electrode springs and pen-nibs (see data in Platinum Metals chapter). Tantalum-nickel alloys are available for use in the electronic field. Tantalum carbide is combined as sintered powder with other carbides and cobalt for use in special cutting tools and dies.

Ferro-alloys

Considerable promise is shown in the application of tantalum and columbium to ferrous metallurgy. Tantalum and columbium in the pure state are expensive, but their ferro-alloys can be prepared inexpensively by silicon reduction. These alloys contain between 50 and 80 per cent of tantalum and columbium, with varying amounts of iron, and traces of tin, manganese, etc.

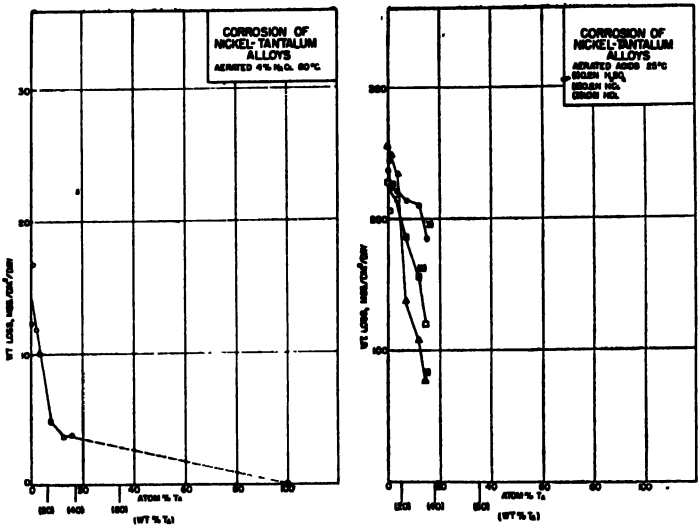


FIGURE 13

Corrosion data for binary nickel-tantalum alloys [Landau and Oldach, *Trans. Electrochem. Soc.*, **81**, 542 (1942)].

Corrosives studied include salt solution and aerated acids. Weight loss is expressed as mg/dm²/day, and alloy compositions are expressed in atomic per cent.

The ferro-alloy is easily added to molten steel. Tantalum tends to oxidize quickly, but columbium does not, and 80 to 85 per cent of the columbium added is retained in cast steel.[38]

When small amounts of ferrocolumbium are added to stainless steel, a product is obtained which shows less intergranular corrosion. It withstands high temperatures and is more easily

welded than ordinary steels. Columbium reduces air hardening, stabilizes impact strength, and improves several other physical properties of 4 to 6 per cent chromium steel.

A recent development is a precipitation hardening alloy which contains iron and 3 per cent columbium. This alloy, which consists of an intermetallic compound, Fe_3Cb_2, exhibits very good rupture strength at elevated temperatures. The metal shows very low creep at high temperatures. This alloy might be used for turbines that are operated at high temperatures.

The small amount of carbon normally present in special steels constitutes a disadvantage, especially in chromium and stainless austenitic steel alloys. It gives chromium steel a tendency toward air hardening and brittleness and encourages grain boundary precipitation of the carbide in austenitic steel, which renders it susceptible to intergranular corrosion. This type of corrosion in stainless steel can be prevented by an initial high temperature heat treatment. However, when the material is welded, some zone of metal near the weld is inevitably heated high enough to reprecipitate the carbide, and at such places susceptibility to corrosion occurs.

Welding Electrodes

The problem of *weld decay* is solved by removing the carbon or putting it into a form in which it will not respond to heat treatment. Tantalum and columbium form extremely stable compounds with the non-metallic elements, and their carbides are not soluble in iron. Hence, they are ideal as preventives of *weld decay* when added to steel in amounts up to 1 per cent, depending upon the amount of carbon present.

Ferrocolumbium is usually used to prevent *weld decay*, either alone or with titanium. It is also a common constituent of welding electrodes which are employed in the fabrication of steels susceptible to *weld decay*. In 6 per cent chromium steels, the presence of columbium increases oxidation resistance

at elevated temperatures, and decreases the period of annealing required to improve their ductility. The properties are also not affected by welding or oxy-acetylene cutting.

Cemented Carbides

When tantalum is added to carbon steel, the iron carbide content is reduced. After hardening this steel by quenching, a new constituent, tantalum carbide, is noted on the uniform martensitic ground mass. In a 1.2 per cent carbon steel containing 18 per cent tantalum, all the carbon is converted into tantalum carbide. The particles of glass-like tantalum carbide are readily recognized under the microscope on the polished surface of the alloy.

By suitable composition control, starting with a material of high carbon content, a steel can be produced which contains a substantial proportion of tantalum carbide. Such alloys are superior for use in high-speed cutting tools. Tantalum carbide ranks among the hardest substances produced by man.* Other metals, including tungsten and chromium, may be added

FIGURE 14
Photomicrograph of tantalum carbide embedded in steel.

* The order of hardness is: diamond, boron carbide, silicon carbide, tungsten carbide, tantalum carbide.

to the alloy for special uses. The resulting alloy consists of a tool-steel matrix, containing a large amount of suspended carbide.

When carbon is added to a melt of ferrotantalum, the melting point of the mass increases. If the pasty mass formed, consisting largely of tantalum carbide, is treated with acids, a fine carbide powder in the form of sharp grains separates out. This powder finds use as an abrasive or as the basis of sintered-carbide alloy tools.

Nitrided Steels

Genders points out that the most interesting feature of tantalum and columbium steels is their behavior when they are surface nitrided in cracked ammonia gas. The commercial alloy steels containing chromium and aluminum are usually subjected to nitriding for about 80 hours at from 480 to 550°C. This treatment forms an extremely hard surface film on the metal which is rich in aluminum and chromium nitrides. These steels are used in automobile and aircraft engine parts which must be practically wearproof.

The addition of tantalum or columbium greatly increases the rate of growth of the nitride layer. As little as 1 per cent columbium gives the full increase in speed of nitriding. A twenty-four hour nitriding treatment gives a hardened layer over 0.3 mm thick and an eight-hour treatment at 550°C gives a layer greater than the minimal commercial specification, which is 0.125 mm.

It is possible to raise the nitriding temperature in columbium steels without embrittlement of the nitrided layer. An increase in hardness results without a diminution of thickness. An initial high-temperature quenching is beneficial for raising the amount of dissolved columbium, and as the steel is free from active carbon, there is no danger of hardening on cooling or cracking. Columbium steels do not oxidize rapidly and can be safely heated to high temperatures, much higher than is possible for ordinary steels.

Other Uses

Pure tantalum was once used for the filaments of incandescent electric lamps. However, it has now been replaced by the development of ductile tungsten. Tantalum and high-tantalum alloys are sometimes used for crucibles and other laboratory ware in place of platinum and its alloys.

A new type of bayonet heater consists of tantalum-protected steel tubes. Tantalum finds application in chemical manufacturing equipment resistant to strong acids (including HCl), nozzles, pump and valve parts, rayon spinnerets, and parts of equipment which must withstand high temperatures and corrosive chemicals.

Copper and steel pipes can be lined with a thin layer of tantalum for corrosion protection. Tantalum-clad apparatus finds some use in the chemical industries. The metal is also used in rectifier plates.

Tyler has described the work of Jefferies,[39] who used sintered tantalum for electrolytic condensers. They have a coarse, porous surface covered with films of tantalum oxide, to give the material its condenser qualities. An important application of these condensers is for lightning and surge arresters in railway signal circuits, especially for the protection of signal lamps.

A small amount of pure columbium and tantalum has been used for special tools. These are made by alloying 50 per cent of either or both of these metals with a non-carbide-forming metal, such as copper or a metal in the platinum group, or a carbide of chromium, uranium, molybdenum, or tungsten, or a metal and a carbide. The resulting alloys may be cast in carbon molds.[39]

The enormous capacity of tantalum and columbium for absorption of all common gases leads to their use in the vacuum tube industry. By employing columbium instead of tungsten or tantalum, it is possible to increase many times the capacity of vacuum tubes.

Analysis of Columbium and Tantalum

Columbium and tantalum are often found together in ores, and both elements closely resemble each other in chemical reactivity. In the gravimetric determination of both elements, the pentoxide is prepared, weighed, and the metal content calculated. The oxides of these metals can be made by igniting columbic and tantalic acids.

Ore Assay

A procedure for the determination of columbium in ores is to fuse 1 g of the finely pulverized mineral, such as columbite, in a platinum crucible with 8 times its weight of potassium bisulfate. High temperatures must be employed to insure complete removal of the columbium. The fusion product is allowed to cool and then pulverized.

The melt is boiled with water so that all the iron, magnesium, and potassium sulfates are extracted, fresh portions of water being used for the extraction. After filtering, the residue of hydrated columbic acid, ferric oxide, stannic and tungstic acids, is digested in ammonium sulfide containing an excess of sulfur. This reagent facilitates solution of stannic and tungstic acids and converts the iron into the sulfide. After filtering, the impure columbic acid is washed with water containing ammonium sulfide and boiled with concentrated hydrochloric acid in order to remove the remaining iron manganese, cerium, uranium, copper, and others which may be present.

The residue after filtering is washed with boiling distilled water. After drying, it is ignited to convert the hydrated columbic acid to columbium pentoxide, which is then weighed. In assaying tantalum the same procedure is employed, including the treatment with ammonium sulfide, and dissolving the impure tantalic acid in dilute hydrofluoric acid in a platinum dish. The solution is filtered, the residue is mixed with sulfuric acid and evaporated to dryness. It is ignited until the

weight becomes constant and allowed to cool in a desiccator. This procedure insures removal of all the silica.

Separation of the Metals

To separate the columbic acid from the residue, the mass is dissolved in hydrofluoric acid, and a boiling solution of acid potassium fluoride added, so that all the tantalum will be converted to potassium fluotantalate and all the columbium to potassium fluoxycolumbate. The solution is evaporated on a water bath and allowed to cool very slowly, the potassium fluotantalate gradually crystallizing out. After filtering, the precipitate is washed with water until the filtrate shows no trace of an orange color with gallic acid solution.

The potassium fluotantalate remaining on the filter is dissolved in hot sulfuric acid and boiled with water to remove the potassium sulfate formed by the decomposition of the fluotantalate. The residue is filtered off, washed, and ignited to tantalum pentoxide.

The quantitative separation of columbium and tantalum is difficult. The previous method is based on the work of Marignac and depends upon the difference in solubility of potassium fluotantalate, which is soluble in from 151 to 157 parts of water, and the solubility of potassium fluoxycolumbate, which is soluble in from 12 to 13 parts of water.

Detection and Analysis

Columbium and tantalum may be detected by preparing a fresh solution from 2 cc portions of 1 per cent sodium thiosulfate, 25 per cent barium chloride, 0.1N acetic acid, and 0.7 per cent hydrogen peroxide. This method is very sensitive, since it depends upon the catalyzed and induced precipitation of barium sulfate by very small amounts of either columbium or tantalum.

The procedure in this test is to divide the reagent into two parts. To one portion add 4 cc of the carefully neutralized solution to be tested, and to the other portion add an equal

amount of distilled water. Shake well and allow to stand. After 15 or 20 minutes the blank test will show a turbidity of sulfur, but if columbium or tantalum is present it will induce the reaction to proceed in another direction, with the precipitation of barium sulfate.

In modifying this test for greater sensitivity, a spot test procedure on black paper may be employed, because the white precipitation shows up much better on a black background. This test is so sensitive that merely stirring the reagent with a tantalum wire will produce the reaction.[40]

The theory behind this test has been discussed by Feigl [41] for several elements. The precipitation of barium sulfate is due to the catalytic action of peracid formers, of which columbium and tantalum are examples, resulting in the development of an acid -O-OH group. The precipitation of barium sulfate will reveal the amounts of peracid formers shown in table 16.

In a similar test, peracid formers activate the hydrogen peroxide-bromide ion reaction. A freshly prepared mixture of hydrogen peroxide, potassium bromide, and methyl orange, which has been acidified with sulfuric acid, is mixed with a peracid forming element. The red solution is decolorized because the bromine liberated in the reaction acts upon the methyl orange, with reformation of the bromide ion. This reaction is exceedingly sensitive.

TABLE 16

PERACID CATALYZED SULFATE PRECIPITATION

Peracid Former	*Identification Limit (Gammas)*	*Dilution Limit*
Columbium	0.2	1:20,000,000
Molybdenum	1.0	1: 4,000,000
Tantalum	0.4	1 10,000,000
Thorium	1.0	1: 4,000,000
Titanium	0.5	1: 8,000,000
Tungsten	2.0	1: 2,000,000
Uranium		See Chapter 5
Vanadium	1.0	1: 4,000,000
Zirconium	1.0	1: 4,000,000

Columbium and tantalum form white, sparingly soluble precipitates with phenylarsonic acid in strongly acid solutions containing tartaric acid.[12] Another test is to treat sodium columbate with ammonium hydroxide, then zinc, and then an acid. A deep-brown color develops, which changes to yellow and is not affected by hydrogen peroxide and ammonium thiocyanate. Titanium solutions treated in the same way yield yellow colorations and when treated with sulfuric acid change to orange.

Columbic acid, treated with potassium hydrosulfate in acid solution, gives a yellow precipitate, and with pyrogallol and gallic acid an orange-yellow precipitate. Tantalum yields a yellowish precipitate. Columbates or tantalates, when boiled with sulfuric acid and phenolic compounds, form characteristically colored solutions.[13]

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CHAPTER V

MOLYBDENUM, TUNGSTEN AND URANIUM

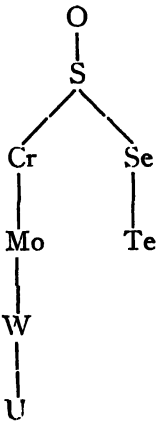
Introduction

Two families of elements make up Group VI of the periodic table. One family consists of oxygen, sulfur, selenium, tellurium, and polonium, and is known as the oxygen-sulfur family (see chapter 6 on Selenium and Tellurium). The other family comprises the metals chromium, molybdenum, tungsten, and uranium. There are marked differences between the two, as may be noted from the accompanying figure, but among elements in each family there are certain resemblances. We are chiefly concerned with molybdenum, tungsten, and uranium in this chapter, although in the strictest sense of the term, these metals should not be considered *rare*. As would be expected, members of the chromium family show a distinct gradation in physical properties with increasing atomic numbers.

TABLE 17

PHYSICAL PROPERTIES OF CHROMIUM FAMILY METALS

Properties	*Chromium*	*Molybdenum*	*Tungsten*	*Uranium*
Atomic weight	52.01	95.95	183.92	238.07
Atomic number	24	42	74	92
Atomic volume	7.7	10.2	9.6	12.7
Specific gravity	7.1	10.2	19.30	18.7
Melting point	1830°C	2625°C	3387°C	1150°C
Boiling point	2260°C	3700°C	4830°C	



Showing the relationship of chromium family metals to the oxygen-sulfur family non-metals.

Molybdenum

History

Molybdenite was known during the time of the Greeks, although in ancient times it was not distinguished from *black lead* (graphite) and galena (PbS). This confusion persisted until the middle of the eighteenth century.* The name *molybdena* is the Greek word for lead. *Plumbago* is the Latin word for graphite and for galena. All three minerals, molybdenite, galena and graphite produce a black streak on paper.

It remained for Scheele [2] in 1778 to prove that molybdenite differs from graphite. He found that when molybdenite was heated with nitric acid, a white residue formed, and under similar treatment graphite remained unaltered. Subsequent studies by Scheele showed that molybdenite is a natural molybdenum sulfide.

Later, Scheele showed that the white residue consisted of an acid-forming oxide, which he called molybdic acid. In 1782 Peter Jacob Hjelm succeeded in isolating the metal by

* Our *lead* pencil increases the confusion; also, in medicine, molybdosis is lead poisoning.

heating the oxide with charcoal. He obtained molybdenum as a fine black powder, but could not fuse it into a button, because the heat obtainable at that time was far too low. In 1893 the French chemist Henri Moissan [1] used the electric furnace to fuse molybdenum. A mixture of the dioxide and carbon were heated at high temperatures and an impure metal was obtained (92 to 96 per cent Mo).

Mineralogy

The principal commercial source of molybdenum is molybdenite, a molybdenum sulfide, MoS_2. The metal is not found in the free state. Molybdenum and tungsten are commonly associated in granitic rocks, but the deposits are not widely scattered. Molybdenite is often found as short, tabular, hexagonal crystals, or as small scales resembling graphite in color and luster. The mineral is very soft, having a Moh hardness of only 1.0 to 1.5; it readily leaves a bluish-gray streak on paper. Molybdenite as mined is usually free from impurities, and when pure it contains 60 per cent molybdenum and 40 per cent sulfur.

Molybdenite is frequently found associated with chalcocite, cassiterite, scheelite, wolframite, fluorite, and other minerals, in pneumatolytic contact deposits in pegmatite and quartz veins associated with granitic rocks. It is more rarely found in granular limestones. The yellow pulverent mineral often seen coating molybdenite in the zone of oxidation is an alteration product, a yellow trioxide known as molybdic ochre.

Molybdenite has been noted disseminated in rock, but not concentrated enough to work the deposit on a commercial basis. Hess has pointed out that tin, nickel, and molybdenum are outstanding examples of mineral deposits which are often lacking in commercial concentration in the United States.[8] The United States is deficient in tin and nickel, but it produces about 80 per cent of the world's molybdenum.

Since 1925, the United States has dominated the world's

production of molybdenum. Most of the metal has come from the Climax Molybdenum Company at Climax, Colorado. In recent years the production of molybdenum at Climax, Colorado has ranged from 25,000,000 to 30,000,000 lb of metal per year. About 35 per cent of the U. S. molybdenum production is now a by-product of several copper mines. There are many important deposits of molybdenite in Canada, but only a few have been fully developed as producers.

In table 18 the best known molybdenum minerals are listed in the approximate order of their importance, together with their composition. Doubtful and unimportant species are omitted.

TABLE 18

PRINCIPAL MOLYBDENUM MINERALS

Mineral	*Composition*	*Per Cent Molybdenum*
Molybdenite	MoS_2	59.95
Wulfenite	$PbMoO_4$	26.15
Molybdite	$Fe_2O_3.3MoO_3 + H_2O$	39.63
Powellite	$Ca(Mo,W)O_4$	47.98
Ilsemannite	$MoO_2.4MoO_3$	68.18
Belonesite	$MgMoO_4$	52.08
Pateraite	$CoMoO_4$	43.85

Other Molybdenum Minerals

Wulfenite, a lead molybdate, is second in importance to molybdenite as a molybdenum mineral. It occurs in veins with other lead minerals, and is most often associated with vanadinite and pyromorphite. In the mines of Arizona and other parts of southwestern United States, it has been found in beautiful crystals. Wulfenite is usually wax-yellow in color but it may be pale brown, bright orange, or reddish. Wulfenite has contributed substantially to the production of molybdenum in the United States.

Molybdite, a molybdic ochre, is a hydrated iron molybdate of variable composition. It has been confused with powellite

in some localities. Molybdite is thought to be formed by a reaction between limonite and molybdic acid, the latter being liberated from the oxidation of molybdenite. It is usually found associated with molybdenite in the upper zone of oxidation.

The presence of the yellow encrustation of molybdite serves as a guide to the prospector, indicating the presence of molybdenum. Outcroppings of the ore may be readily traced in this manner.

Powellite, a mixture of calcium molybdate and calcium tungstate, usually contains about 10 per cent tungstic oxide, and may readily be identified by its characteristic dull-yellowish fluorescence. It is often found in the zone of oxidation in deposits of molybdenum and tungsten. Hence, a single hand specimen may show molybdenite, scheelite, and powellite.

Ilsemannite, while not important as a source of molybdenum, may serve the prospector as an indicator for molybdenite. It is a blue-black mineral, soluble in water, which leaves a bluish stain on the surrounding rock. When molybdenite weathers, it sometimes becomes tinged with this bluish color.

Physical Properties

Pure massive molybdenum is a silvery-white metal which resembles tungsten in some of its physical properties. Osmium, tantalum, rhenium, and tungsten are among the few metals with higher melting points than molybdenum. It is quite malleable, softer than steel (having a Moh hardness of 5.5 to 8.5), and is not sufficiently hard to scratch glass. It is used as a target in X-ray tubes.

The appearance of molybdenum metal depends largely on its preparation. Crude, gray molybdenum, an electric furnace product made directly from molybdenite, is made up of approximately 92 per cent molybdenum, 2 per cent iron, and 6 per cent carbon. This impure furnace product is brittle, having a hardness greater than that of quartz. Small amounts of

impurities render molybdenum both brittle and non-ductile. Molybdenum that can be drawn into fine wire, ribbons, and rolled into thin sheets can also be produced. The tensile strength of molybdenum wire is about one-half that of tungsten wire.[4]

TABLE 19

PHYSICAL PROPERTIES OF MOLYBDENUM

Property	*Value*
Atomic weight	95.95
Atomic number	42
Atomic volume	10.2
Specific gravity	10.2
Melting point	2625°C
Boiling point	3700°C
Thermal expansion at 20° C	5.25×10^{-6}
Specific resistance	4.77 microhms
Specific heat	0.0647 cal.
Latent heat of vaporization	170 Cal. gram-atom at b.p.
Thermal conductivity	0.350 cal/cm² sec
Moh hardness	5.5-8.5
Isotopes	7
Crystal	Cubic, body-centered
Tensile strength	140-217 kg/mm²

Molybdenum alloys with several metals, especially with iron. Molybdenum steels have several properties which make them valuable for the manufacture of various tools and machine parts. Molybdenum also alloys with nickel to form a metal highly resistant to elongation under tensile stress.[5]

Chemical Properties

Pure molybdenum is not attacked by water, and exposure to air at ordinary temperatures does not affect it. However, when the metal is heated it turns brown, then blue, and finally, a white oxide coating forms. The metal is resistant to the action of the halogen acids and dilute sulfuric acid, but it dissolves in concentrated sulfuric acid and in aqua regia. It is oxidized by nitric acid to the trioxide. Molybdenum is slowly

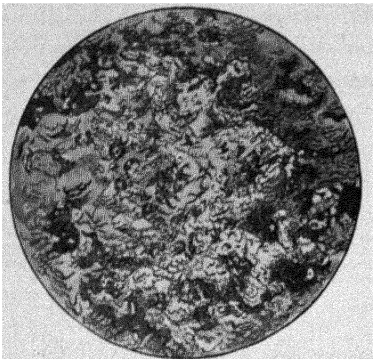


FIGURE 15
Structure of cold-worked molybdenum, magnified 200X (courtesy of Westinghouse Research Laboratories).

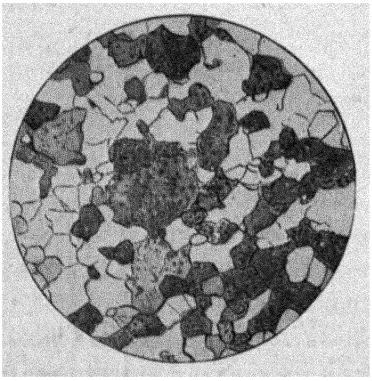


FIGURE 16
Structure of annealed (recrystallized) molybdenum, magnified 300X (courtesy of Westinghouse Research Laboratories).

attacked at room temperature by halogen gases and it is slowly soluble in fused sodium hydroxide. Fused sodium peroxide also acts on molybdenum.

Compounds

Molybdenum forms six oxides: the black monoxide, MoO; the sesquioxide, Mo_2O_3; the dioxide, MoO_2; the blue molybdenum oxide, Mo_3O_8; the hemipentoxide, Mo_2O_5; and the pale yellow trioxide, MoO_3. The trioxide, a white to pale yellowish solid, is the most stable and has the most salts, dissolving in alkali hydroxides to form molybdates. Molybdenum is not known to form any basic radicals. Four chlorides are known but they are not true salts. They are either complexes or volatile covalent compounds.

Probably the most interesting quality of molybdates is that they tend to form poly-compounds. That is, many of the compounds are derivatives of complex acids, such as heptamolybdic acid. To illustrate this, consider that molybdenum trioxide combines with phosphorus pentoxide to form at least seven of the less complex phosphomolybdates in the following ratios of P_2O_5 to MoO_3: 1:24, 1:22, 1:20, 1:18, 1:16, 1:15, 1:5.

Nitric and hydrochloric acids precipitate white molybdic acid, H_2MoO_4, from solutions of the molybdates. Molybdic acid dissolves in an excess of the reagent. Hydrogen sulfide or ammonium sulfide causes the precipitation of molybdic trisulfide from acid solution. This compound is soluble in alkaline sulfides and sulfo salts.

Probably the characteristic reaction of molybdic acid, or molybdic anhydride, is the precipitation from nitric acid solution of the bright yellow phosphomolybdate or arseniomolybdate when only traces of soluble phosphate or arsenate are present. Molybdic acid can be prepared from ammonium molybdate by the action of nitric acid; it forms yellow crusts which give sols with water.

Molybdic trioxide can be obtained from molybdenite by roasting. It forms ammonium molybdate with ammonium hydroxide and can be purified by this reaction. When ammonium molybdate is ignited, the trioxide is formed. With alkalis,

molybdic acid forms molybdates which have a tendency to condense to the poly-acids mentioned before.

Extraction from the Ore

The process employed for extraction of molybdenum depends on the ore. Molybdenum salts are generally obtained from molybdenite by roasting and dissolving the residue in ammonium hydroxide or another base. With a good grade of ore, molybdenum trioxide of high purity may be obtained by roasting.

For minerals such as wulfenite, it may be necessary to fuse the ore with potassium sulfide and extract the crude molybdenum sulfide with water as the sulfo salt. Upon acidifying the filtrate, the lead sulfide remains as an insoluble residue. The molybdenum sulfide is precipitated and subsequently treated like molybdenite by roasting.

Ferromolybdenum

For the production of ferromolybdenum an electric furnace is used. The metal is obtained from molybdenite, sodium molybdate slag, calcium molybdate, or molybdic oxide. A reducing agent, such as carbon or ferrosilicon containing 90 per cent silicon, can be employed. A flux of fluorspar or lime is usually added to make the slag fusible.

In recent metallurgical operations calcium molybdate has partly replaced ferromolybdenum. Calcium molybdate is superior because it is less expensive and no carbon contaminates the resulting alloy. To prepare calcium molybdate, the molybdenite concentrate is roasted with 0.25 per cent sulfur in a multiple hearth roaster, the last hearth having calcium hydroxide added to it. Calcium molybdate is formed in the process and obtained as large solid fragments which are broken up before distribution.

Preparation of the Metal

Molybdenum metal may be prepared in several ways. Usually the ammonium compound, ammonium molybdate, is decomposed at red heat in an atmosphere of hydrogen to a fine, dark powder of elemental molybdenum. The same treatment may be given other salts or the trioxide. Chlorides may also be reduced by hydrogen.

Aluminothermic reduction has been used with success for preparing molybdenum metal, although in large scale operation the method is expensive. Usually the dioxide is heated with aluminum powder.

In electrothermic reduction to molybdenum, the trioxide prepared from ammonium molybdate by ignition is mixed with about one-tenth its weight of carbon. This mixture is then heated in an electric furnace.

Technology

Ferrous Metallurgy

Molybdenum increases the elongation of steel very considerably. For wire drawing and other applications such an increase at a comparatively small cost is important. It also renders tool steel especially hard and capable of retaining a cutting edge. Molybdenum steel is used for making rifle barrels, propeller shafts, and special machine parts.

Molybdenum steels are not like ordinary carbon steels, since they retain their temper when heated to relatively high temperatures. Thus it is possible to make high-speed tools from molybdenum steel, because the metal can be heated to dull redness without impairing its cutting edge or temper.

The first military tanks used in France during World War I were armored with heavy manganese steel castings more than 3 in. thick. These were readily penetrated by the high-powered German armor-piercing projectiles. The 3-in. manganese steel plate was replaced by nickel-molybdenum armor of 1-in. thick-

ness, which apparently withstood the severe tests with armor-piercing shells.

Authentic statements regarding the use of molybdenum steel during World War I are lacking, but there is no doubt that molybdenum steel was employed in tools and machine parts. It was reported that the huge German howitzers used against Liége and Namur owed their extraordinary endurance to a lining of molybdenum steel inside the barrel. Analysis of captured guns showed that molybdenum was not present, but the steel barrels did contain about 3 per cent nickel and over 1 per cent chromium. During the latter part of World War I, molybdenum steel was used for the manufacture of various types of armor shielding made in the United States, but it is doubtful whether this metal saw actual battle service.

There are a number of ferromolybdenum alloys available which vary in molybdenum content from 60 to 80 per cent, and contain from a few tenths to 2 or 3 per cent carbon, according to the process by which they are made. Ferromolybdenum is also manufactured with 85 per cent molybdenum and only about 0.2 per cent carbon.

Molybdenum steels in certain fields have proved superior to tungsten steels. It has been found that molybdenum steel is easier to harden than tungsten steel. Ferromolybdenum goes into solution when added in small amounts to steel. Molybdenum steels have a fine-grained structure. They have been employed recently in cracking stills and high-pressure boilers. These steels resist creep or elongation at elevated temperatures.

Bray [6] has pointed out that nitriding steels also contain molybdenum, which inhibits grain growth and intergranular weakness during the nitriding treatment. They give a tougher nitrided case and improve the strength of the finished product. Molybdenum can be added in small amounts (from 2 to 4 per cent) to stainless steels to enhance resistance to corrosion. When added to stainless steels, molybdenum also imparts other desirable physical qualities to the alloy. It is significant in that

for certain applications the addition of 8 or 10 per cent molybdenum to high speed steels provides a worthy substitute for tungsten, since nearly twice that amount of tungsten would be required (the density of W is 19.3, of Mo is 10.0).

Molybdenum steels of special formula are acid-proof steels. Hence, they are of particular value to the chemical industries. An alloy containing 60 per cent chromium, 35 per cent iron, and 2 or 3 per cent molybdenum is barely affected by dilute hydrochloric, nitric, or sulfuric acids, or even by boiling aqua regia.

When ferromolybdenum is mixed with cast iron, the product has greater strength and the large graphite particles are broken down into small particles. Such molybdenum iron is harder and has greater resistance to wear and rough handling. It is claimed that the machinability of this iron is improved, as well as its impact resistance.

Non-ferrous Metallurgy

Like that of vanadium and tungsten, the non-ferrous metallurgy of molybdenum is comparatively undeveloped. There are a number of molybdenum alloys besides those with iron, principally the alloys with nickel. Several molybdenum-nickel alloys are produced commercially, one of which, for example, contains 75 per cent molybdenum and 25 per cent nickel. Another alloy is made up of 50 per cent of each metal.[7]

The percentages of constituents in these alloys may vary slightly, according to the impurities present in the products, as for example, from 2 to 2.5 per cent iron, 1 to 1.5 per cent carbon, and 0.25 to 0.50 per cent silicon. A chromium-molybdenum alloy, containing no carbon is made up of 50 per cent of each metal and is a market commodity. It is prepared by aluminothermic reduction.

Uses of Pure Molybdenum

Pure molybdenum finds little use in industry, but its few

applications are very valuable. An outstanding application is in the manufacture of anti-cathodes for X-ray tubes. Molybdenum wire has found extensive use for the support of tungsten filaments. The metal and its alloys may be used for electrical contacts, spark plug electrodes, filaments, and screens and grids for radio tubes. The alloys of nickel-chromium-molybdenum find limited use in heat resistors. Pure molybdenum is being used widely in the form of flat ribbons for heating elements in the high-temperature electric resistance type of furnace. In an atmosphere of hydrogen the furnaces operate successfully up to 2000°C.

Uses of Molybdenum Compounds

Molybdenum compounds are much like those of vanadium and tungsten so far as their technology is concerned. Little use has been made of the numerous molybdenum compounds. Sodium molybdate is used in ceramics for coloring pottery and porcelain and for dying silks and woolens. The same compound may be used in the dye industry as a mordant. It is also found in ink formulas. Molybdenum-lake dyes are fast to light and resist the action of water and many mild chemical agents.

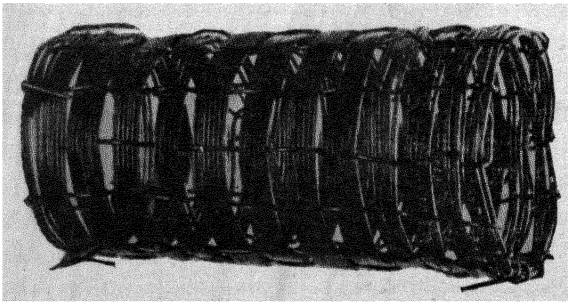


FIGURE 17
Molybdenum resistor furnace element.

Ammonium molybdate is an important reagent for phosphate analysis, but its consumption for this purpose is small.

The same compound has been used for fire-proofing and as a bactericidal agent. Molybdenum tannate with hematoxylin extract finds some use in leather coloring and dyeing. Molybdenum *indigo* has found limited application as a pigment for india rubber.

Lead molybdate and certain other heavy metal derivatives of the same anion may be employed for opacifying glass and for preparing enamels. Such enamels have great covering power and a low fusing point, thus being superior to the analogous tin products. Molybdic acid is used for the determination of phosphorus, phosphates, and lead. This compound is also used in glazes for ceramics.

Analysis

There are many methods for the determination and detection of molybdenum. Spectrochemical technique allows accurate qualitative and quantitative determinations on only a few milligrams of specimen. Microchemical methods can also be employed and these are gaining favor, particularly in studies on trace amounts of the element.

Molybdenum can be weighed as the oxide obtained from the ignition of ammonium molybdate, the mercury salt, or the salts obtained from precipitation with organic reagents. It is also possible to convert the sulfide into the oxide with nitric acid and estimate the element gravimetrically. In the volumetric determination of molybdenum, soluble molybdates are reduced by boiling with potassium iodide, and the liberated iodine is measured by the standard thiosulfate method.

Micro Tests

Several microchemical tests for molybdenum have been developed by Martini.[8] In one, 0.1 to 1 per cent ammonium molybdate solution is added dropwise to a saturated solution of pyrocatechol acetate until an orange color forms. Aniline is then added, with care to avoid an excess. In positive reac-

tions myriads of small triclinic crystals form. If the small amount of aniline used is replaced with piperazine, crystals of the same color but of a different crystalline form will appear.

To a drop of 1 per cent ammonium molybdate solution small amounts of pyrocatechol are added until the liquid becomes a deep red-orange. A very small drop of benzylamine is then added, followed by a drop of 15 per cent acetic acid, with rapid stirring. Groups of orange crystals form.

Moir [9] acidifies the alkaline solution with acetic acid and adds hydrazine sulfate. Upon boiling, a blue color forms if molybdenum is present. Or, the solution may be acidified with acetic acid and potassium iodide added. Upon boiling, a blue color forms if molybdenum is present.

The addition of a small amount of pyrogallol to a molybdenum-containing solution acidified with acetic acid causes the solution to turn red-orange.

In the Pozzi and Escot test, the neutral solution is treated with 1 drop of a saturated solution of mercurous nitrate, 1 to 1.5 cc of concentrated hydrochloric acid, and an excess of potassium iodide. This mixture is shaken so that the greenish mercurous iodide dissolves. If tungsten or molybdenum is present, a blue color quickly forms. The color soon disappears and iodine separates out.[10] Molybdate solutions can be moistened on filter paper or a spot plate with sulfuric acid and cautiously heated until the acid has evaporated. The residue is ultramarine blue.[11]

For the Zaffuto test, the solution is acidified with nitric acid, ammonium nitrate and 1 cc of alcohol added and the solution shaken. Crystals of sodium hydrosulfite are then added, and if the reaction is positive the solution becomes brown, then greenish-blue, and on shaking and heating at 60°C, a dark blue color forms.[12]

Phenylhydrazine Tests

Phenylhydrazine is a good reagent for the detection of small amounts of molybdenum. An extremely sensitive test for the

element is made by adding a saturated solution of phenylhydrazine to the solution to be tested, together with hydrochloric acid. In positive reactions a red or rose color forms, with as little as 1 part in 2,500,000.[13] When the acid is absent a red-brown precipitation takes place.

One test for molybdenum uses freshly distilled phenylhydrazine as the reagent and 1 g in 70 cc of 50 per cent acetic acid. It is claimed to be able to detect 1 part in 1,000,000 of the metal.[14] The procedure is to boil 10 cc of the solution to be tested with 5 cc of the reagent for 2 minutes. If molybdenum is present a red color develops. If the coloration is not distinct a small amount of chloroform is mixed with the solution so that the red color is extracted, becoming easily visible. Other elements, such as tungsten, vanadium, arsenic, antimony, chromium, tin, iron, manganese, or uranium, do not give this reaction.

Other Reactions for Molybdenum

In the Bertrand reaction[15] for molybdenum, the reagent is prepared by dissolving 11.4 g of ammonium tungstate in 20 cc of water, and an equal amount of 20 per cent aqueous sodium hydroxide. Gentle warming may be necessary to insure complete solution. Seventy cc of 30 per cent tartaric acid solution are added, together with 5 cc of hydrochloric acid and enough water to dilute to 0.5 l. This solution is then thoroughly saturated with hydrogen sulfide for 30 minutes and allowed to stand for 12 hours. After filtering, the hydrogen sulfide is boiled off, the reagent cooled, and then diluted to 2 l with water.

To make the test, the molybdate solution is diluted to about 50 cc, 6 cc of 1:1 hydrochloric acid, 2 cc of 1:1 phosphoric acid, and 5 cc of the reagent are added. This solution is diluted to 80 cc and 10 cc of stannous chloride solution are added. The stannous chloride solution is prepared by dissolving 20 g of pure tin shot in 200 cc of hydrochloric acid, and diluting to 1 l. In the presence of molybdenum, a light-blue to deep violet-blue coloration forms.

When a slightly ammoniacal solution containing molybdic

acid is added to hydrogen peroxide, a red-brown coloration forms.[16] As little as 1 gamma of molybdenum in dilutions ranging up to 1 part in 4,000,000 can be detected by peracid-catalyzed sulfate precipitation, as described in chapter 4.

In the Braun reaction[17] for molybdic acid, a granule of zinc is added to the solution, then a few drops of potassium thiocyanate solution and hydrochloric acid is added drop by drop, so that a slight evolution of hydrogen occurs. In positive reactions a carmine-red color forms with as little as 1 part molybdenum in 300,000.

When ethyl acetate is added to a solution of molybdenum in hydrochloric acid in the presence of a 25 per cent sodium thiosulfate solution, the ethyl acetate becomes pale violet, reddish, or red-brown depending upon the amount of molybdenum present. The test is sensitive to about 1 part in 1,000,000.[18]

In the Jaffe reaction,[19] several cubic centimeters of the solution to be tested are acidified with hydrochloric acid, and triethanolamine slowly trickled down the side of the test tube. In positive reactions, a green ring forms at the liquid surface, gradually turning turbid. A blue precipitate then forms, which is soluble in an excess of the reagent and partly soluble in water.

Molybdenum is precipitated from slightly acid solutions by an alcoholic solution of α-benzoinoxime.[20] In another test,[21] 2 drops of a 3 per cent alcoholic solution of α, α′-dipyridyl are added to the unknown solution, followed by a drop of stannous chloride (a 50 per cent solution in concentrated hydrochloric acid). An intense violet coloration forms if molybdenum is present, although tungstates interfere. The test is sensitive to 1 part in 100,000.

Molybdenum can be detected by evaporating the solution to be tested to dryness with nitric acid, extracting the residue with ammonium hydroxide, and filtering. The filtrate is neutralized with hydrochloric acid and potassium thiocyanate added. The red coloration which may be due to iron is shaken

out with ether. Zinc and hydrochloric acid are added until gas begins to evolve. A bright red color forms if as little as 1 part molybdenum in 50,000,000 is present.[22]

In Lecocq's test [23] a violet or indigo color forms when an alcoholic solution of diphenylcarbazide is added to a solution of ammonium or sodium molybdate, acidulated with hydrochloric acid. The reaction does not take place in the presence of excess alkali.

TUNGSTEN

History

Fundamental work on both molybdenum and tungsten was done by the Swedish chemist Scheele. Before the discovery of tungsten, which means *heavy stone* in Swedish, a dense mineral now known as scheelite, was taken for tin stone (cassiterite). However, in 1781, Scheele showed that the mineral contained lime (calcium oxide) and a new acid. This was shown to be a metallic compound by Bergmann. In 1783, the two Spanish chemists, the D'Elhujar brothers, showed that the same acid discovered by Scheele was present in wolframite.

Mineralogy

Tungsten is not found native, but certain minerals contain simple compounds of the metal in comparatively high percentages. Tungsten is widely distributed, but only a few localities are commercial sources for the metal. Like the ores of molybdenum, those of tungsten are frequently associated with granitic rocks in quartz formations, commonly in conjunction with cassiterite, topaz and apatite.

Some of the tungsten minerals, especially scheelite, may be found with gold and silver ores. Recently, some low-grade gold ore was discarded as worthless, but on reexamination with ultraviolet light, it was found to contain commercially valuable quantities of scheelite and other tungstiferous minerals.

There are numerous localities in the United States where

tungsten minerals are found, but during peacetime few of these deposits can be worked in competition with foreign deposits. The result is that little attention is given the domestic deposits until an urgent demand is created by war. In World War I, considerable work was carried out in the tungsten deposits of Boulder County, Colorado, and elsewhere in this country where tungsten was known to occur, but after the end of hostilities these domestic deposits could not compete with the much cheaper Chinese ores.

While the present production of tungsten in the United States is not sufficient to supply the increased demand under war conditions, it is possible that with intensive prospecting and development of known properties, a sufficient domestic supply may become available. During the past few years the production of tungsten in Nevada, California and Colorado has increased enormously.

In 1940, during diamond drilling of an antimony property in the Yellow Pine, Idaho, district, an unsuspected deposit of scheelite was discovered mainly through fluorochemical examination (depending on fluorescence under short wavelength ultraviolet light) of drill core. Additional drilling has revealed that the tungsten deposit is extensive and contains at least 100 million dollars' worth of this vital metal.

This discovery was the most spectacular geological revelation of the year. In the Salmon, Idaho, district, prospecting with ultraviolet light has revealed the presence of large deposits of powellite and cuproscheelite. Scheelite will probably be encountered in exploration at depth, the powellite and cuproscheelite appearing near the surface in the zone of oxidation.

Scheelite

Scheelite, $CaWO_4$, is by far the most important tungsten mineral mined in the United States, much of the present supply coming from California and Nevada. The recently discovered scheelite deposit in Idaho, however, may exceed that of any

other single property in this country. Scheelite is found scattered in localities in numerous other Rocky Mountain states.

When pure, scheelite contains about 86 per cent tungsten oxide. It lacks metallic luster, but can often be identified by its high specific gravity of approximately 6. Its color is usually similar to that of massive white quartz, and in the hand sample it is nearly impossible to distinguish it from quartz by visual examination.

While scheelite is generally found in massive or crystalline form disseminated or bunched in the matrix, colorless crystals of high purity are sometimes encountered.

Fortunately, pure scheelite fluoresces a strong and characteristic blue under short wavelength ultraviolet light, the presence of molybdenum altering the emission to white or yellow. Portable ultraviolet light units, operated from dry cell batteries are now being widely used in prospecting for scheelite outcroppings. Fluorochemical technique is also used in mining the ore underground, and in milling operations. In milling, the heads and tailings are tested, and an experienced operator can judge the recovery with accuracy, eliminating many slow and costly wet assays.

Other Tungsten Minerals

The most notable deposits of ferberite in the United States are in Boulder County, Colorado. During World War I these deposits made important contributions to the domestic tungsten supply.

Ferberite, $FeWO_4$, is black in color and has a specific gravity of about 7.25. In the mines of Colorado, ferberite is often stained with coatings of limonite or iridescent chalcopyrite. Some of the finest crystals known have come from the mines of this region. Ferberite is often found associated with huebnerite.

Powellite is an alteration product of scheelite in which some of the tungsten has been replaced with molybdenum. It is dull yellow in color, and is frequently seen as a coating and filling

in cracks and vugs. Powellite is often associated with scheelite, often serving as an indicator for scheelite in the zone of oxidation.

Huebnerite is pure or nearly pure manganese tungstate, $MnWO_4$. It generally has a reddish-brown color and is quite opaque, with a specific gravity approximately the same as ferberite. Some varieties of huebnerite contain iron and tend to gradate into wolframite. Ferberite and huebnerite are considered varieties of wolframite when the manganese and iron contents pass a certain limit.

Wolframite is usually black in color, with a specific gravity near that of huebnerite and ferberite. In the mines of the United States, wolframite occurs rather sparingly, but some foreign mines yield wolframite as the dominant tungsten mineral. It is said that some foreign users prefer wolframite, since this ore requires less fluxing in the process of reduction.

One of the characteristics of all tungsten minerals is their high specific gravity, hence they are often recovered in placer operations. Small water-worn pebbles of tungsten minerals can frequently be recognized because of this quality. Hand panning of placers is also used to sample the ground and to trace the source of tungsten minerals in the search for commercial ore bodies.

The better known tungsten minerals and ores are given in the approximate order of their commercial importance in domestic deposits in table 20.

Physical Properties

Pure tungsten is a steel-gray metal with a bright metallic luster and the highest melting point of any known metal; solid tungsten liquefies at 3387°C. Tungsten has a high tensile strength and other properties which make it very valuable in the metallurgical industries. Tungsten is a dense metal, its specific gravity of 19.30 being exceeded only by that of rhenium, iridium, osmium, and platinum. The specific gravity of tungsten is approximately equal to that of gold.

TABLE 20

PRINCIPAL TUNGSTEN MINERALS

Mineral	*Composition*	*Per Cent WO_3*†
Scheelite	$CaWO_4$	71–86
Ferberite	$FeWO_4$	69–82
Powellite	$Ca(Mo,W)O_4$	10–11
Huebnerite	$MnWO_4$	73–82
Wolframite	$(Fe,Mn)WO_4$	74–82
Cuproscheelite	$(Ca,Cu)WO_4$	76–79
Tungstite	WO_3	98–100
Stolzite	$PbWO_4$	Variable *
Cuprotungstite	$(Ca,Cu)WO_4$	56–57
Raspite	$PbWO_4$	Variable *

* Pure lead tungstate contains 50.96 per cent WO_3.
† Pure WO_3 contains 79.31 per cent W.

The combination of high fusing point and electrical resistivity make tungsten ideal for incandescent filaments, as well as for resistor wire in electric furnaces. Under bombardment by electrons, tungsten emits X-rays useful in medical and industrial radiography. In construction of anticathodes for X-ray tubes, the high melting point of tungsten again plays an important role.

Tungsten has a thermal coefficient of expansion close to that of Pyrex glass and therefore it can be used for electrical lead-ins and for metal-to-glass joints and welds.

TABLE 21

PHYSICAL PROPERTIES OF TUNGSTEN

Property	*Value*
Atomic weight	183.92
Atomic number	74
Atomic volume	9.6
Specific gravity	19.30
Melting point	3387°C
Boiling point	4830°C
Thermal expansion at 20°C	4×10^{-6}
Specific resistance	5.48 microhms
Specific heat	0.034 cal
Latent heat of vaporization	217 Cal/g atom at b.p.
Thermal conductivity	0.476 cal/cm²/sec
Moh hardness	4.5 to 8.0
Heat of fusion	4.4 cal/g

Although tungsten in massive form is almost white, the

metal may be prepared as a very hard powder ranging in color from gray to brownish-black, resembling tin, and sometimes iron. On fusion sintered tungsten becomes bright, although direct melting is a very difficult problem due to the lack of a container with a melting point appreciably higher than the melting point of tungsten.

One of the chief characteristics of tungsten is that it readily alloys with iron (see the section on tungsten technology). Tungsten also alloys with many other metals to give products having unusual physical properties. When tungsten combines with non-metals, such as carbon, unique substances are formed.

Tungsten is readily taken up by steel to form a hard, compact, and heat-resisting alloy which is self-hardening on continued use. An unusual property of tungsten steel is that it is capable of taking a very high degree of magnetization. It resists corrosion, damascenes finely, and withstands the deleterious effects of sea water.

Chemical Properties

Pure tungsten is resistant to the action of most single acids, but a mixture of nitric and hydrofluoric acids dissolves it easily. The powdered metal dissolves in boiling potassium hydroxide solution and to a lesser extent in other alkaline reagents. Upon solution in potassium hydroxide, hydrogen gas is evolved and potassium tungstate forms. Tungsten is not affected at ordinary temperatures by air or halogens, but when heated to redness, the halogens attack it. Fused potassium nitrite and similar chemicals dissolve tungsten.

Compounds

Tungsten exhibits four valences: two, four, five and six. These are exemplified by the chlorides. Tungsten forms four oxides: WO, WO_2, W_2O_5, and WO_3, of which the latter is the most important. The compounds of tungsten are similar to those of molybdenum, although the relationship is less close

than that between tantalum and columbium. Like molybdenum, tungsten combines with phosphorus pentoxide to form complex condensed poly-acids, of which at least six are known, i.e., those having a P_2O_5 to WO_3 ratio of 1:22, 1:21, 1:20, 1:16, 1:12, 1:7.

Like those of molybdenum, the highest oxides of tungsten are most stable, and the trioxide is the outstanding compound, forming tungstates. Tungstic acid and tungsten trioxide can be reduced to the dioxide by many reducing agents.

Tungstic acid is a yellow or greenish-yellow powder which is insoluble in water and acids, except hydrofluoric acid, but is slowly soluble in alkalis. When freshly precipitated from a soluble tungstate, it is white, contains 1 molecule of water and is appreciably soluble in water. Tungsten trioxide, on the other hand, is a heavy amorphous, canary yellow powder which becomes dark orange when heated, and regains its original color on cooling.

Production of Metallic Tungsten

The principal world source of tungsten in recent years has been wolframite, which is magnetic due to its iron content. In view of this fact, magnetic separation can be employed for concentrating and processing wolframite. The ore may be treated with fused sodium carbonate and then leached with water. The filtrate is acidified with hydrochloric acid and tungsten trioxide obtained as the precipitate. Upon dissolving this in ammonium hydroxide, ammonium tungstate forms, from which a pure trioxide is obtained by repeated precipitation with hydrochloric acid and resolution in ammonium hydroxide. Finally, the WO_3 is subjected to reduction by hydrogen.

Elemental tungsten may also be obtained by heating tungstic acid with carbon, heating the hexachloride in hydrogen, or heating the nitride. The oxide, WO_3, when heated with metallic zinc, also yields tungsten metal. A more recent process, however, is to electrolyze a fused mixture of tungstates. When

a relatively impure product can be used, carbon reduction usually suffices.[24]

At the present time, there are two main commercial processes for the production of metallic tungsten of high purity. In the Shoppler process, high-grade scheelite is fused with sodium carbonate after being finely ground and intimately mixed. The fusion product is granulated and the sodium tungstate formed is leached out with water.

After filtering and washing, the clear solution is treated with hydrochloric acid. The granular precipitate of tungsten trioxide is recovered after the solution has been carefully boiled for several hours to prevent colloidal precipitation, which interferes with processing.

FIGURE 18

Tungsten treating furnaces at the General Electric Research Laboratory.

The oxide is carefully dried and reduced, with a calculated amount of carbonaceous material, to the metal in a special furnace at 1250°C. Tungsten metal is obtained in about 4 hours as a lumpy, porous, gray mass, which is screened and packed for shipment.

In the Fansteel process, wolframite is heated at 800°C with sodium carbonate in a small reverberatory furnace. The sodium tungstate formed during the reaction is extracted with water. To the filtered and clear tungstate solution, calcium chloride is added, precipitating the tungsten as calcium tungstate. After washing and treating with hydrochloric acid, the trioxide is obtained. Tungsten metal powder is obtained by reduction in hydrogen at 1200°C.

Ferrotungsten

Carbon reduction is employed to a large extent for making ferrotungsten by reducing wolframite directly with carbon in an electric furnace. The pure metal is also obtained by reduction of the trioxide with a calculated amount of charcoal in an electric furnace. The procedure is to mix one part oxide with about 12 per cent charcoal and 5 per cent pitch rosin. Tungsten separates out as a dense white metal.

The production of ferrotungsten is accomplished by incorporating a specified amount of tungsten ore with iron oxide or iron scrap. The tungsten and iron are then charged with charcoal, glass, and quartz or other flux and smelted at high temperatures. The ferrotungsten collects in the bottom of the furnace, and after solidification the furnace is dismantled and the button lifted out.

Technology

The Incandescent Filament

One of the best known uses for tungsten is in the incandescent lamp filament. Tungsten possesses physical properties which make it suitable for making into metal filaments for electric

lamps which must withstand high temperatures and rough handling. The metal does not melt below 3300°C and it has a comparatively low vapor pressure at the operating temperature (2300°C). Tungsten, both hot and cold, has sufficient strength

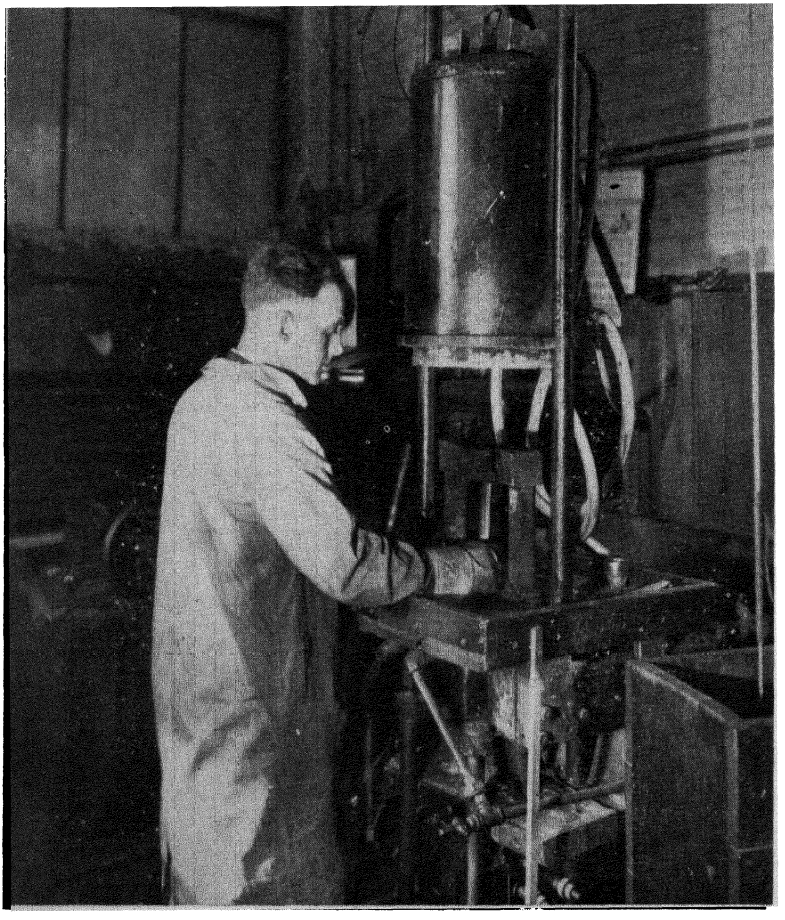


FIGURE 19

Treating bottle used at the General Electric Research Laboratory for sintering tungsten.

to be used as a filament when drawn to a diameter as small as 0.0005 in.

Before 1908 tungsten was considered a non-ductile metal. The story of how its brittleness was overcome is interesting. The research through which tungsten was first produced in ductile form was performed by Fink and Coolidge, two investigators of the General Electric Co., who worked independently but employed similar methods. Briefly, in the production of ductile tungsten, powdered tungsten of exceptional purity is specially swaged, heat treated, and drawn to wire of the desired dimensions. The tungsten used for incandescent filaments must be obtained by hydrogen reduction, so that iron and other metallic impurities are eliminated, rather than by carbon reduction, which suffices for alloying purposes. The presence of traces of foreign metals in tungsten renders it unsuited for

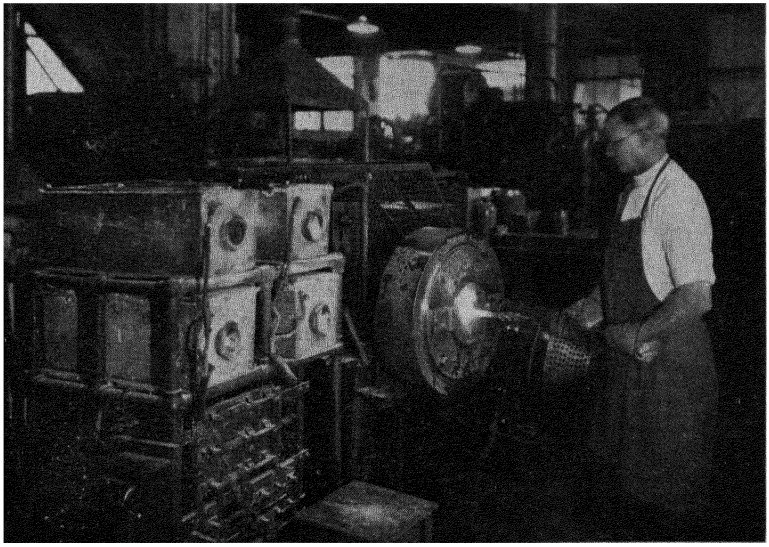


FIGURE 20
Swaging tungsten at the General Electric Research Laboratory.

the production of filament wire as the resulting product is too brittle to withstand long life and rough handling.

In the General Electric process for the production of ductile tungsten, the metal powder obtained by sintering is hydraulically compressed into bars. The bars are heated to a high temperature (3300°C) in an atmosphere of hydrogen, yielding a strong but very brittle product. This is converted into rods by a hot hammering process in which the metal, previously heated to 1500°C in an electric furnace, is subjected to ten thousand blows per minute in a special swaging machine. Reduction to fine wire is accomplished by drawing the rods through dies. Tungsten wire can be drawn to 0.011 mm, and by immersion for 45 seconds in a fused mixture of sodium nitrate and sodium nitrite at 340°C, a uniform reduction of the wire from 0.014 to 0.007 mm is obtained.[25]

In another process for the production of ductile tungsten, a small amount of a substance, such as 1.4 per cent zirconium and 2 to 3 per cent copper, is incorporated into a rod of tungsten metal. On heating this rod in pure hydrogen, a product is obtained which is ductile and capable of being drawn into filaments which are relatively soft and non-sagging.[26]

Tungsten Steel

As long ago as 1860 Mushet found that small amounts of tungsten hardened steel, but it remained for Taylor, at the turn of the century, to direct attention to the advantages of high-speed steel made with tungsten. The Mushet type of tungsten steel contained from 5.5 to 9.0 per cent tungsten and enough manganese to give it air-hardening properties.

Tungsten is added to steel in the form of ferrotungsten alloy. Ferrotungsten is made, like ferrochrome, by the direct reduction of high-grade ore in an electric furnace. Ferrotungsten alloys vary in tungsten content according to their application. Usually, however, the approximate limits of tungsten in ferrotungsten are between 30 and 80 per cent. Over 90 per cent of

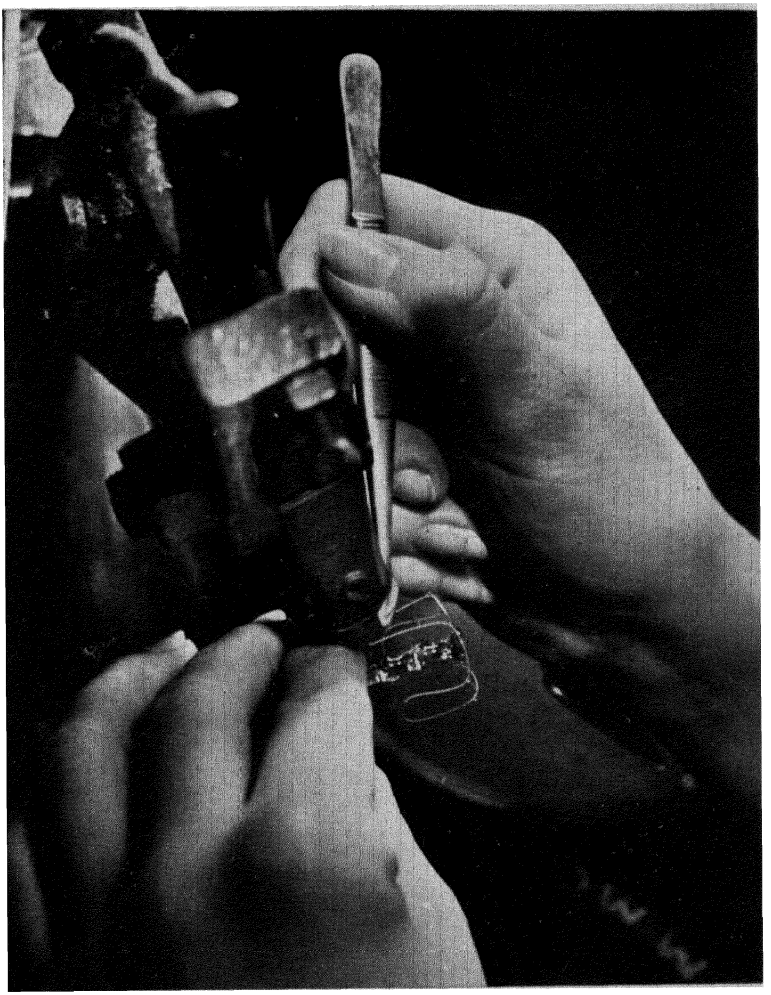


FIGURE 21

Construction of tungsten filament element by hand at the Westinghouse Research Laboratory.

the total tungsten consumed is in the steel industry. Tungsten filaments use up less than 5 per cent of the tungsten.

When ferrotungsten is added to steel, the final tungsten content generally varies between 3 and 18 per cent, depending on the nature of the steel to be prepared. It is occasionally as much as 24 per cent, but the usual amount is about 3 per cent. The carbon content varies between 0.4 and 2 per cent. Taylor-White tungsten steel, for example, contains 8.5 per cent tungsten and from 3 to 4 per cent chromium; it has been made in two grades, one for cutting soft steel and gray cast iron, and the other for cutting hard steel. The tungsten content of both grades remains constant, but there is 1 per cent more chromium in the grade used for cutting hard steel than in that employed for cutting soft steel.

Tungsten steels are very hard and compact and are not impaired by the heat generated at high cutting speeds. Ferrotungsten is readily dissolved in molten steel and when large amounts of the alloy are added, the steel becomes so hard that it is workable only with special cutting tools on lathes and milling machines and must be forged or ground. The atoms of tungsten, being much heavier and larger than those of iron, diffiuse comparatively slowly in the solid metal, so that a high temperature is required before the quench. The accumulation of carbide particles upon tempering is also slow, hence the ability of these particles to hold their hardness at high temperatures. In keen-edged tools, tungsten seems to prevent the small particles from being torn away during use and thus retards dulling.

Steel containing 0.9 per cent carbon or more and from 1 to 2 per cent tungsten is used extensively in hack saw blades, reamers, broachers, and similar tools which must exhibit minimal changes in dimension after heat treatment. Steels containing 1 per cent or more carbon and 3 to 7 per cent tungsten are used for fast finishing tools to cut hard metals or make a fine, smooth cut on softer but tough metal.

Dies are made from tungsten steel for cold drawing wire. This steel contains 2 per cent carbon and from 1 to 12 per cent

tungsten. Greater amounts of tungsten are added to alloys which go into the dies used for drawing harder metals and finer wire.

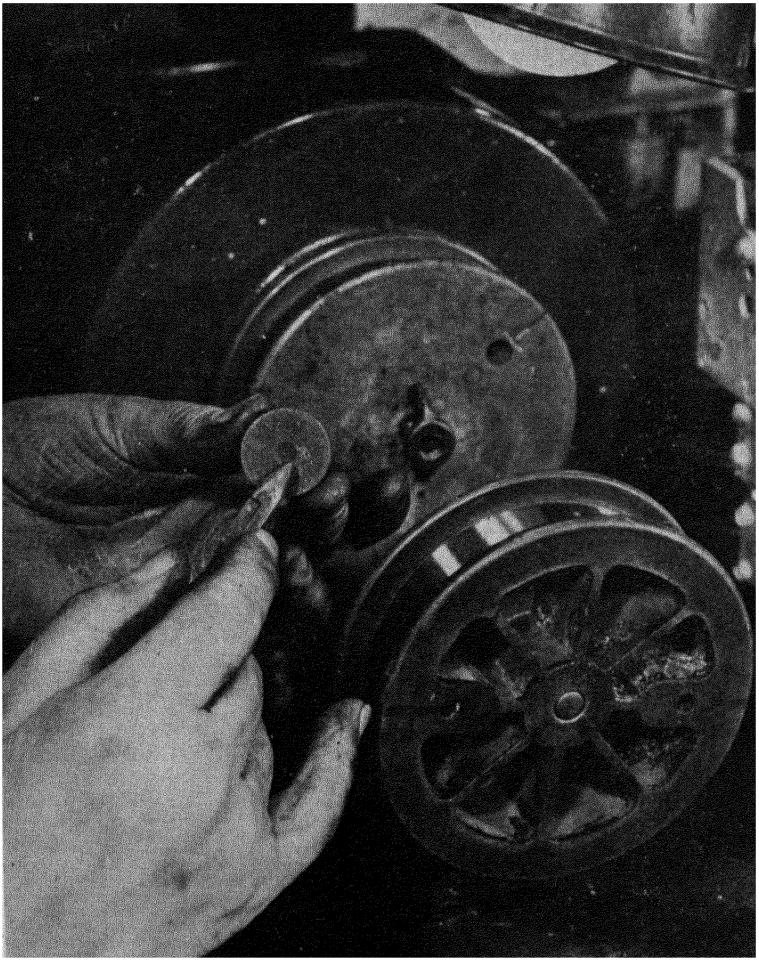


FIGURE 22

Diamond die for drawing tungsten wire, at the Westinghouse Lamp Division.

Chromium is added to tungsten steel to enhance diffusion of the tungsten. Amounts between 0.5 and 7 per cent cause cracking in water hardening, but oil quenching will harden the metal through the center.

The value of tungsten steel is in its ability to retain strong magnetism. This quality makes tungsten steel particularly desirable in instrument work, where calibration depends on the permanence of the magnet used. For compass needles, tungsten steel is very dependable, but the most important use of magnetic tungsten steel is in permanent magnets for radio and communication devices. These alloys usually contain 0.7 per cent carbon and from 5 to 6 per cent tungsten.*

Other Alloys

Many other alloys of tungsten have been developed. For example, the cobalt-chrome-tungsten alloys or stellites used for cutting tools. An alloy of nickel and tungsten can be introduced into steel, imparting the properties of both tungsten and nickel. Tungsten-nickel generally carries about 75 per cent of the former metal and 25 per cent nickel. Steels containing small amounts of vanadium, ferrotungsten, and/or nickel-tungsten have remarkable physical characteristics and find use in armament manufacture. The addition of manganese and/or copper into such alloys also produces valuable changes in physical properties.

Several tungsten-aluminum alloys have been developed for the airplane industry. Copper-aluminum-tungsten alloys may be made into propellor blades. An alloy of aluminum and tungsten has been prepared for automobile construction. The alloy is said to be light and possess a high tensile strength, increased hardness, and greater elasticity. Such a metal may be cast and made into profiled sections and sheets.

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* Recently the far superior permanent magnet Alnico has largely displaced the tungsten steel magnets.

Cemented Tungsten Carbide

Tungsten carbide is now being used as a cutting agent and abrasive. Tungsten carbide is among the hardest substances known, either natural or artificial, melting at about 2500°C. Its utility is limited because of its brittleness.[6] To overcome this, cemented tungsten carbide is prepared by embedding in the carbide small percentages of a metal such as cobalt or nickel. Other metal carbides have been used in conjunction with that of tungsten, i.e., the carbides of tantalum, columbium, vanadium, and titanium (see chapters 3 and 4). Cemented-carbide types of cutting tools and agents have been developed in the last few years and have opened a new branch of technology. A typical cemented-carbide alloy is made up of 43.5 per cent tungsten carbide, 43.5 per cent tantalum carbide, and 13 per cent binding alloy.

Uses of the Tungstates

The commercial applications of tungstates are numerous. For instance, sodium metatungstate, $Na_2W_4O_{13}.10H_2O$, is employed in fire protection. When combustible materials have been treated with a solution of this compound they do not burst into flame, but only smolder slowly. Sodium tungstate is used as a mordant in dyeing. Lead tungstate is used in place of white lead and the bright-yellow tungsten trioxide finds some application as a pigment in oil and water colors.

Special treatment of the alkali metatungstates gives rise to various pigments which have a beautiful, metallic luster. These are used as *bronzes*. To prepare such pigments, polytungstates are treated with sodium hydroxide and hydrochloric acid and then fused with tin.

Potassium metatungstate subjected to the action of an electric current gives deep-blue coppery crystals of a hydrated tungsten suboxide. When tungsten trioxide is added to fused potassium until it is no longer taken up and the mass gently heated in a current of hydrogen and digested with water,

striking violet crystals form. This substance is known as magenta bronze.

Saffron bronze may be prepared in the same way except that sodium is used instead of potassium. The crystals have a less complex composition, but they are very useful. It is reasonable to assume that an entire series of bronzes can be developed in this manner, by substituting other light metals for the potassium or sodium. Lithium, cesium, rubidium, calcium, magnesium, and even beryllium may form new and beautiful pigments.

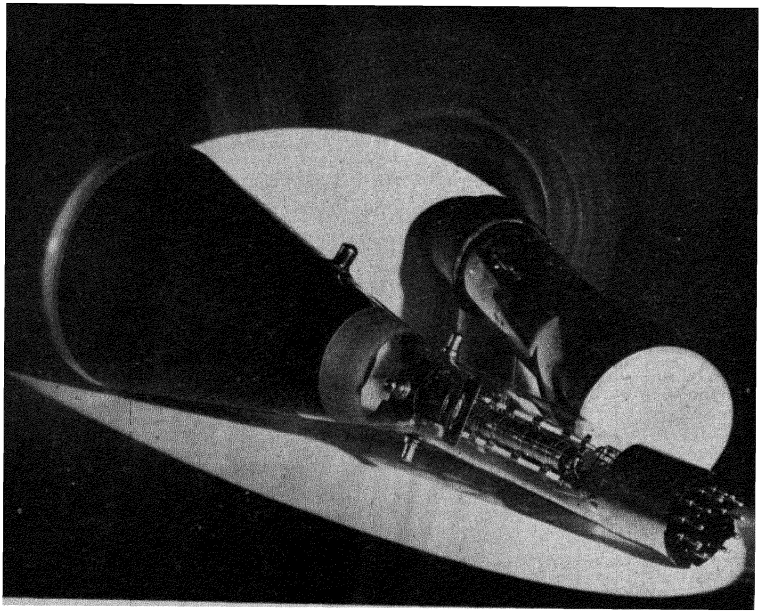


FIGURE 23

Cathode ray tubes with luminescent tungstate screen (courtesy of Allen B. Du Mont Laboratories).

Other Applications

Special tungsten alloys have been used for contact points in electrical apparatus, vacuum tubes, wireless apparatus, communications equipment, phonograph needles, etc.

Fluorescent tungsten compounds have been employed in X-ray screens for fluoroscopy. The intensifying screen used in radiography contains a coating of calcium tungstate over its surface.

Tungstate phosphors are now finding wide application in lighting tubes and luminescent paints. Details for the preparation of various tungstate paints and phosphors which glow in the dark have been given.[47] Tungstate phosphors may be used for coating television tube screens, in electronics research, and in the electron microscope.

Tungsten salts are similar to those of vanadium. Tungsten compounds are used for the manufacture of stained paper products. Their use for making non-combustible goods should be extended. Some tungsten compounds are used in the so-called "dry" fire extinguishers, but they are expensive. Tungsten has also been used in ceramics for coloring and opacifying glassware and porcelains.

Analysis

The tungsten in ores is ordinarily determined as the trioxide, which can be obtained by ignition of the tungstates of ammonium or mercury, by the decomposition of alkali tungstates with nitric acid, or by boiling lead tungstate with hydrochloric acid.

Ore Assay

A simple method for the quantitative assay of tungsteniferous ore is to reduce the sample to a fine powder and digest 1 g with a mixture of 4 parts hydrochloric acid and 1 part nitric acid for 12 hours, or until a yellow powdery tungstic acid residue remains. The solution is evaporated to dryness and acidulated

with hydrochloric acid. After filtering, the residue is washed with alcohol. It usually contains silicates and traces of columbic acid as impurities. The mixture is filtered and treated on the filter with ammonium hydroxide. The filtrate is placed in a large tared porcelain crucible and evaporated to dryness on a water bath. The residue, consisting of ammonium tungstate is ignited and weighed as the trioxide, from which the weight of the metal is calculated.

Tungsten may be detected in ores by treating 0.2 g of the powdered sample with a small lump of zinc and heating for 2 minutes with hydrochloric acid. If tungsten is present a blue color forms, and on adding 15 cc of water a blue, flocculent precipitate appears. If only small amounts of tungstate are present, or if the reduction is carried further, the precipitate becomes green or brown. If water is not added after boiling with acid, a bluish-red solution is obtained. When the hydrochloric acid is evaporated off, blue tungsten pentoxide forms, and the solution is yellow from tungsten trioxide. As little as 0.5 per cent tungsten may be detected.[27] The Pozzi and Escot [10] test described in the section on molybdenum analysis may also be used for tungsten in ore.

In assaying tungsten ore it is essential not only to determine the percentage of tungstic oxide, but also the phosphorus, sulfur, tin, arsenic, and silicon content.

A very good test for tungsten, molybdenum, titanium, and vanadium in ores has recently been developed by Van Valkenburgh and Crawford at the University of Colorado. Harrison has used this test with considerable success.[56] Powder the sample finely, fuse it with an excess of ammonium hypophosphite, and note the color which develops in the melt on cooling with or without the addition of small amounts of water. After fusion, cobalt, titanium, and tungsten color the fusion product blue. A red coloration is due to vanadium and is enhanced when small amounts of hydrogen peroxide are added.

Dropwise addition of water to the hot melt results in a change in color from blue to violet in the presence of tungsten. The

color is evident in a short time in the presence of large amounts of the metal, but for traces of tungsten a period of from 10 to 30 minutes may be required before the violet color is visible.

A simple test has been found satisfactory by Harrison [56] for the rapid detection of scheelite, and perhaps other tungsteniferous substances. The procedure is to dissolve the finely powdered sample in concentrated hydrochloric acid and dilute with an equal volume of water. The addition of metallic zinc or tin results in the formation of a characteristic blue color when tungsten is present.

A rather complicated test for tungsten in ore has been developed and employed by Heath.[28] However, in a simple version of the test, 5 g of finely ground sample are digested by boiling with 25 cc of nitric acid, the addition of hydrochloric acid being necessary when the ore does not decompose easily. After diluting with water, the solution is filtered, and the filtrate mixed with from 5 to 10 cc of glacial acetic acid, the acid being poured slowly down the side of the tube. In the presence of tungsten, a characteristic red ring forms below the solid precipitate.

Steel Analysis

In determining tungsten in steel, 2 g of the metal to be analyzed are dissolved in a mixture of equal parts sulfuric and phosphoric acids with 1.5 l of water. To this solution there are added, from time to time during solution, 3 cc of potassium permanganate solution. When the solution becomes cold, it is divided into aliquot parts. To one portion 200 cc of 1 :3 sulfuric acid are added, together with 40 g of zinc shavings.

The solution is heated and allowed to cool in a stream of carbon dioxide. Any excess zinc is filtered off, and the filtrate titrated against standard permanganate solution. In the second portion, iron is determined by the Reinhardt method, or with stannous chloride and iodine, and the tungsten estimated by subtraction.

When concentrated hydrochloric acid is added to a tungstate

solution until the precipitate which forms is redissolved and then metallic zinc added, the mixture develops a characteristic color. Usually the coloration is magenta red. But if potassium thiocyanate is used instead of zinc the mixture becomes green and on dilution it turns violet.[29]

Other Reactions for Tungsten

Tungstates, molybdates, and vanadates may be detected simultaneously with a reagent consisting of 1.5 g of tetramethyldiaminodiphenyl methane dissolved in 300 cc of water, together with 10 cc of glacial acetic acid. This solution is filtered and dilute ammonium hydroxide added dropwise until a faint opalescence develops. It is then refiltered. When molybdate solutions are added to this reagant, a blue precipitation occurs; with tungstate solutions, opalescence is noted; a yellow precipitate, gradually turning green, develops on addition of the reagent at a pH of 3.5 to a neutral vanadate solution.[30]

Tungstates may be detected by placing a drop of the solution on filter paper which has been moistened with hydrochloric acid. In the presence of tungstate, a yellow stain due to tungstic acid forms. The coloration becomes blue when ammonium thiocyanate and stannous chloride solutions are added; this is intensified with more hydrochloric acid. As little as 4 gammas of tungsten in 10 microliters of solution can be detected.[31]

When a solution of a tungstate is acidified with sulfuric acid and potassium ferrocyanide added, a greenish-yellow to dark orange-yellow color develops. With stannous chloride a white precipitation occurs; with zinc a blue color forms.[32]

The Fluorochemistry of Tungsten Minerals [37]

In the last few years, the fluorescence of certain tungsten minerals has been made use of in prospecting, mining, and milling tungsten ores. There has been a difference of opinion

regarding the fluorescence of scheelite and other luminescent tungsten minerals. Some writers have stated that scheelite fluoresces only a strong medium blue under short wavelength ultraviolet light, whereas powellite and cuproscheelite fluoresce variable shades of pale yellow under the same radiation. It has been agreed, however, that these natural phosphors are not excited to fluoresce characteristically by long wavelength radiation.*

FIGURE 24

Ultraviolet prospecting for tungsten ores (courtesy of Ultra-Violet Products, Inc.)

* The Mineralight lamp, made by Ultra-Violet Products, Inc., Los Angeles, California, is generally accepted as the best ultraviolet unit for tungsten work.

In the past, the molybdenum content of scheelite tungsten ore could be determined effectively only by chemical analysis. However, with investigations at the laboratories of the U. S. Geological Survey in 1942, the fluorochemical method has been improved to the degree that it may be used to determine accurately the molybdenum content of commercial scheelite. Although pure scheelite fluoresces a characteristic blue, small amounts of molybdenum alter the emission from blue to white to yellow. When the fluorescence is white, the scheelite contains roughly from 0.35 to 1.0 per cent molybdenum and when the scheelite fluoresces a distinct yellow, the ore contains more than 1 per cent. Since scheelite concentrate containing more than 0.4 per cent molybdenum is subject to price penalty, the value of this quick method for estimating molybdenum becomes apparent.

In the improvement of the fluorescence analysis of tungsten minerals, chemists at the Survey prepared synthetic ore containing varying amounts of molybdenum and tungsten. Table 22 gives a resumé of the results obtained, showing the effect of varying proportions of molybdenum on the fluorescence of scheelite. These results, checked by chemical analysis on samples from various localities, were in close agreement.

TABLE 22

FLUORESCENCE OF TUNGSTEN MINERALS

2537 Å Excitation

Mineral	*Per Cent Mo*	*Fluorescence*
Scheelite	Negligible	Strong blue
Scheelite	Traces	Paler blue
Scheelite	0.35–1.0	Strong white
Scheelite	> 1	Yellow
Scheelite	4.8	Strong yellow
Powellite		Strong yellow
Cuproscheelite		Yellow

As might be expected, the fluorochemical method for detecting and inspecting tungsten ores is especially valuable for night prospecting. The Survey has prepared a series of synthetic tungsten minerals comparable to those encountered in the field. Each member in the series contains known amounts of molybdenum incorporated in a base of pure calcium tungstate (scheelite). In the series, pure calcium tungstate is followed in sequence by compounds containing 0.05, 0.19, 0.33, 0.48, 0.72, 0.96, 1.4, 2.4, 3.4 and 4.8 per cent molybdenum, and finally by a standard containing pure calcium molybdate, which is 48 per cent molybdenum.

The samples are made in card form so that alternating with the circles covered with powder, are circular holes of the same size. The card is placed over a finely powdered sample taken from the field. The sample, seen through one of the holes, will be found to fluoresce a color and hence have a composition between that of two adjacent standards. The composition can be further narrowed down by observing which of the standards the sample more nearly resembles. The accuracy of the determinations can be increased by mounting a greater number of standards on the comparison card.

De Ment's Drill Core Method [33]

It is of interest in connection with the discussion of the fluorescence of tungsten minerals to note that drill core from any type of mining, construction, or prospecting operation may be examined by fluorochemical means. The technique has already been used with great success for locating large bodies of tungsten minerals. A good illustration of its usefulness is the recent discovery of ore in the Salmon, Idaho district by means of fluorochemistry.

Uranium

History

In 1789 Klaproth showed that pitchblende partly dissolved in aqua regia. When a clear cold solution of pitchblende was added to an alkali, an unknown yellow precipitate formed. The addition of sulfuric acid produced a lemon-yellow sulfate, and nitric acid produced a greenish nitrate.

Klaproth showed that the unknown substance contained neither chromium, zinc, iron, nor tungsten, but an entirely new element. He named this new element *uranium* in honor of Herschel's discovery of the planet Uranus in 1781.

After Klaproth's discovery, other chemists confirmed the existence of the new element. In 1791 Richter published a paper on uranium and in 1805 Bucholz studied the substance. Klaproth unsuccessfully attempted to prepare elemental uranium by reduction. Despite this, it is very interesting to note that Klaproth termed his element *half-metallic*, although it was not until about 150 years later that studies on its crystalline structure by advanced methods indicated that uranium is a pseudo-metallic element.

Isolation of Uranium [34]

It was not until 52 years after its discovery that pure uranium metal was isolated. In 1841 Peligot showed that Klaproth, instead of obtaining the pure element, had only prepared a lower oxide, the dioxide, when he reduced the yellow oxide by sugar charcoal. Peligot prepared metallic uranium by reduction of uranium chloride with potassium in a platinum crucible.

On several occasions Moissan attempted to prepare metallic uranium. In 1893 he made an impure uranium metal by reducing uranium oxide, U_3O_8, with sugar charcoal in an electric furnace. The product contained large amounts of carbon and other impurities. In 1896 Moissan tried to produce uranium

metal by electrolysis of the double sodium uranium chloride in an atmosphere of hydrogen, using carbon electrodes. The uranium produced by this technique consisted of a spongy mass containing small metallic crystals.

Mineralogy

Uranium ores are comparatively rare, and the primary ores, like pitchblende, are invariably associated with granitic rocks. The secondary uranium minerals, like carnotite, are derived from the weathering of primary ores, and may be found associated with granitic rocks, or they may be water-transported to sedimentary formations. Hence, in prospecting for ores of uranium, the granitic rocks and granite pegmatites offer the best possibilities. Aside from the carnotite deposits of Colorado and Utah, most of the world's uranium ores are found with granitic rocks.

Classification of Uranium Ores[35]

The United States Bureau of Mines classifies the uranium ores into three general types:

1. Uraninites
2. Columbium-titanium tantalates of the rare earths and uranium
3. Secondary uranium minerals

Type 1

The uraninites, which are the richest in uranium, include crystalline varieties such as broeggerite, cleveite, and nivenite. These varieties occur in pegmatites and often in well-developed crystals. Pitchblendes are amorphous uraninites occurring often in metalliferous veins and associated with various sulfides, including silver, iron, lead, cobalt, zinc, and other metals. The term *uraninite* and *pitchblende* are often used synonymously, but the latter term is generally applied to the amorphous and impure forms of the mineral.

Pitchblende often occurs with botryoidal surfaces and a characteristic conchoidal fracture. It is black or grayish-black in color, often with a glossy or pitch-like luster. The pitchblende of Great Bear Lake, Canada, has a brownish-black color on the freshly broken surface. The hardness of pitchblende is approximately that of steel (5.5), while the specific gravity varies with the purity and ranges from about 5 to 9.7.

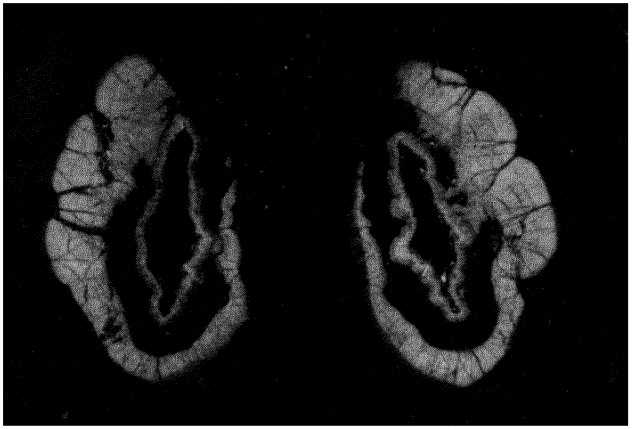


FIGURE 25

Radiograph of two halves of a sawed nodule of high grade pitchblende, El Dorado Mine, Great Bear Lake, Canada (courtesy of Hugh S. Spence, Canada Bureau Mines).

Type 2

The uranium minerals of this group are of complex chemical composition, often well crystallized, occur in pegmatite dikes, and generally have a specific gravity of over 4. They are usually dark brown or black in color.

Type 3

The secondary uranium minerals are all derived from the alteration or decomposition of primary uranium minerals, and may occur in both igneous and sedimentary formations. The various secondary minerals include phosphates, carbonates, arsenates, sulfates, silicates, vanadates, and uranates of uranium. Most of them are characterized by bright colors. Being formed relatively recently, many of the secondary minerals have not yet reached equilibrium, as indicated by the uranium-radium ratio. Carnotite, autunite, and torbernite are typical of this group.

TABLE 23

URANIUM MINERALS [35]

Mineral	*Per Cent* U_3O_8
Ampangabeite	14–20
Autunite	60
Betafite	20–30
Blomstrandite	20
Broeggerite	77
Carnotite	61–67
Chalcolite	55–60
Cleveite	57–72
Curite	Up to 73
Euxenite	3–19
Fergusonite	2– 9
Gummite	60–70
Johannite	66
Liebigite	37–38
Pitchblende	75–95
Samarskite	3–16
Thorianite	5–12
Troegerite	66.3
Uraninite	See pitchblende
Uranophane	52–65

Pitchblende

Pitchblende (uraninite) is a complex oxide of uranium containing variable amounts of lead, iron, copper, bismuth, and the rare elements radium, thorium, yttrium, helium, and argon.

Radium was first discovered in pitchblende. Uraninite crystallizes in the isometric system, but crystals are rare, the mineral usually occurring in a massive or botryoidal form. Depending

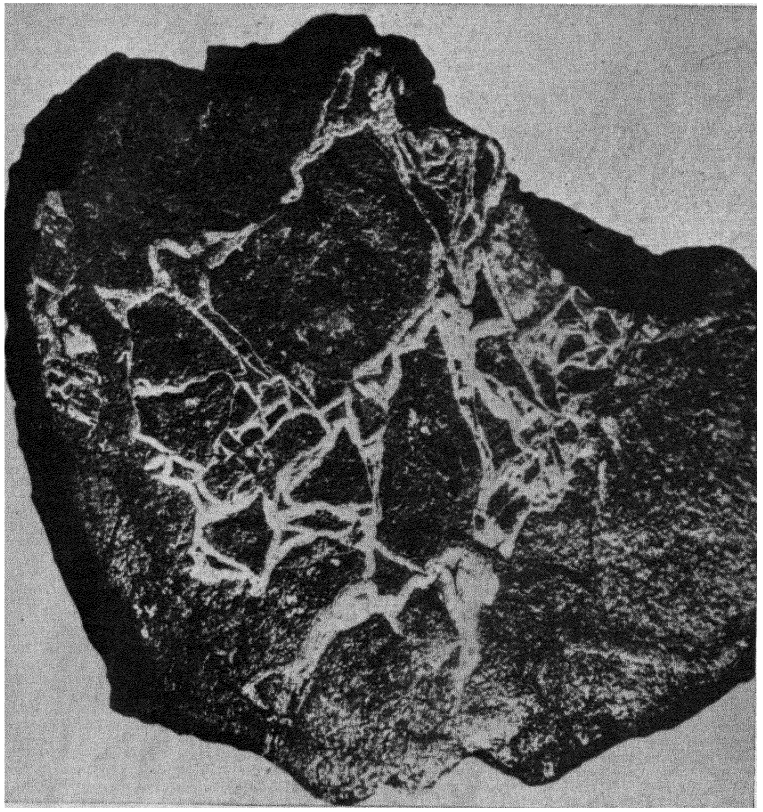


FIGURE 26

Pitchblende veins in an ore specimen from the El Dorado Mine, Great Bear Lake, Canada.

upon the purity, the percentage of uranium oxides in pitchblende varies from about 64 to 89 per cent.

Pitchblende is an extraordinary mineral. In it helium was

first discovered, by Ramsay in 1895. The radioactive elements uranium, radium, polonium, and actinium were also first discovered in pitchblende. It is also used to manufacture plutonium. The discovery and isolation of uranium and radium, in turn, led to many important discoveries and advances in chemistry and physics. The conception of the atom has greatly changed since the discovery of these radioactive elements. Pitchblende is variable in composition, hence its several modifications have different names, such as cleveite, nasturan, nivenite, and broeggerite.

Commercial deposits of pitchblende are few. They include those of Great Bear Lake, Canada, the Belgian Congo, the Joachimsthal district of Czechoslovakia, and scattered deposits of lesser importance in other parts of the world. According to Spence, the Great Bear Lake pitchblende is the richest known considered-as-tonnage grade of ore. The Great Bear Lake deposits are also the most extensive.

The widely distributed pegmatite dikes of the New England states yield small, isolated, quantities of pitchblende. Pitchblende in acicular crystals has been reported from the Rathgeb mine, near San Andres, Calaveras County, California. Wyoming, Colorado, Nevada, and other states have reported isolated occurrences of pitchblende. The nivenite variety of uraninite was mined at Barringer Hill, Llano County, Texas, a locality now inaccessible.

Carnotite

Carnotite is an amorphous, soft, powdery mineral, sometimes talcose or waxy in character. The color is generally a bright canary-yellow, but it may be discolored by iron oxides, organic matter, or other substances. Carnotite is essentially a hydrous potassium-uranium vanadate, having a hardness of from 2 to 2.5, and a specific gravity of from 3.5 to 3.9.

Although uranium and vanadium are chemically unlike, they occur together in carnotite, and both are generally recovered

in the treatment of the ore. Vanadium is a member of the phosphorus group of elements, while uranium is more like tungsten and molybdenum. Vanadium is more common to the ferromagnesian rocks, while primary uranium minerals occur in granites and pegmatites; the secondary uraninites, like carnotite, may occur in both granitic rocks and sedimentary formations. Carnotite was first described by Friedel and Cumenge in 1899. It is widely distributed in the sandstones of the plateau region of southwestern Colorado and southeastern Utah, where it occurs in rich masses and as an impregnation, filling interstices between grains of sandstone, and in cracks

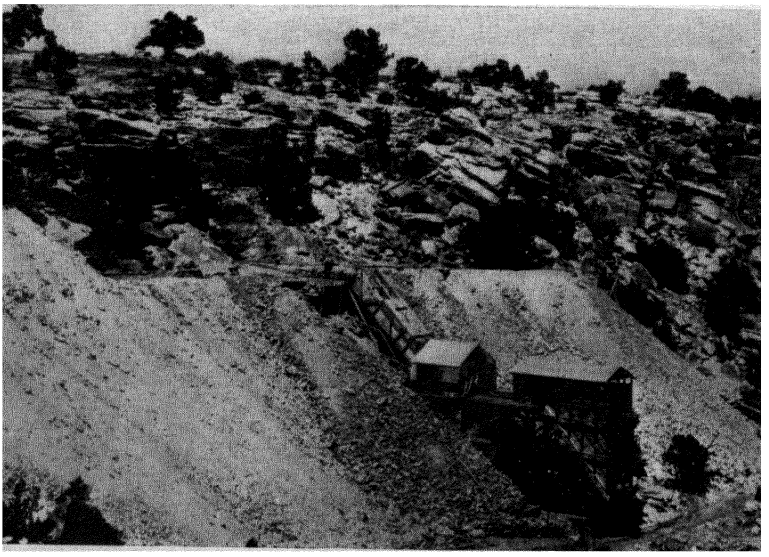


FIGURE 27

Uranium workings in Colorado locality (courtesy of A. D. Riley)

View of a dump of the Club Camp workings in Heiroslyphic Canyon, lower San Miguel River, Montrose County, Colorado, producing uranium and vanadium.

and crevices. Typical analysis of carnotite from Montrose County, Colorado, shows the presence of 54 per cent of uranium oxide, and an average of 18 per cent vanadium oxide. Carnotite rarely occurs without the association of other uranium and vanadium minerals.

The origin of the carnotite deposits of Colorado and Utah has been a matter of speculation. It appears certain that the bodies of carnotite were formed after the deposition of the sandstones in which they occur. Field evidence also points to the conclusion that the carnotite could not have resulted from the alteration of other uranium minerals originally contained in the sands. The shape and position of the deposits indicate clearly that the uranium and vanadium minerals contained in the sandstones have been transported by water to their present place. Some of the rich areas of carnotite represent areas of concentration from material already disseminated in the sandstones. It is quite possible that the great carnotite deposits of Colorado and Utah were derived from extensive primary uraninite deposits in granitic rocks, of which there remains no trace. As an analogous instance, attention is called to the deposits of dakeite in the gypsite found north of Wamsutter, Wyoming. Unquestionably, the dakeite, a secondary uraninite, was derived from the alteration of uraninite from the adjacent granitic rocks and water-transported to its present position in sedimentary deposits.

Carnotite is found at a number of localities in the world and in the United States outside of Colorado and Utah, but the latter deposits are the only ones which have been commercially exploited. Prior to the discovery of rich uranium ores in the Belgian Congo, the Colorado-Utah deposits were extensively mined, primarily for their radium content. In 1913 Colorado and Utah produced about 2,700 tons of carnotite ore, containing over one million dollars' worth of radium. Over 6,000 tons of ore were produced in 1939.

Other Uranium Minerals

Autunite is one of the most widely distributed and important of the secondary uraninite minerals. It is frequently associated with pitchblende, forming coatings and filling crevices on pitchblende and the adjoining rocks. It is commonly found in pitchblende-bearing pegmatites throughout the world. Autunite is a phosphate of uranium and calcium, containing from 55 to 62 per cent uranium oxides. It may be distinguished by its yellowish-green color and powerful yellow-green fluorescence under ultraviolet radiation. When some of the calcium in autunite is replaced by barite the mineral becomes uranocircite.

Samarskite is rather abundant in the United States. It is sometimes found in large masses at the mica mines in Mitchell County, North Carolina. Large crystals were found in the Fridlund mine near Petaca, New Mexico, and described by Hess in 1930. The samarskite of Petaca occurs in a pegmatite dike and is composed of two parts, an older part about 300,000,000 years old, and a younger part, which has partly replaced the older mineral, about 150,000,000 years old. It contains from 10 to 15 per cent uranium oxide, U_3O_8.

Zippeite, a hydrated uranium sulfate, averaging 68 per cent uranium oxides, occurs as a coating on pitchblende ores at Great Bear Lake, Canada. Curiously enough, the zippeite at Great Bear Lake does not appear on the ores within the mine workings, but develops on the ore dumps outside the mine. Zippeite occurs with carnotite in Colorado, and as powder with gypsite near Fruita, Utah.

Physical Properties

Uranium in massive form is a lustrous, white, malleable metal capable of taking a high polish. It has a specific gravity of 18.68 at 13°C. Pure uranium is highly ductile, but small amounts of iron and aluminum in it cause embrittlement. Electrolytic uranium is embrittled by the presence of as little as 0.2 per cent aluminum or 0.5 per cent iron.

The physical properties of uranium are given in table 24. It is to be pointed out that present interest in the nuclear physics of uranium centers on its isotopes, their separation, and their possibilities as sources of energy.

Powdered uranium is gray to black in color, and can be made into buttons and wire. The powdered uranium is pressed into cylindrical buttons, heated until the metal fuses (about 1150°C), and separated from the residue. The residue consists mostly of oxide. It is very difficult to determine the metal content of uranium powder, because of the presence of occluded gases and the variable oxide content due to the reactivity of the metal.

TABLE 24

PHYSICAL PROPERTIES OF URANIUM

Property	*Value*
Atomic weight	238.07
Atomic number	92
Atomic volume	12.84
Specific gravity at 13°C	18.68
Melting point	1150°C
Atomic heat at 0°C	6.57
Specific heat at 0°C	0.0276
Resistivity at 20°C	0.00006 ohm-centimeter
Rockwell hardness	B92–B94, fused
Usual color, massive	White with bluish tint

Uranium wire is made from buttons by cold rolling. When about 50 per cent reduction in cross section has been brought about, the wire is annealed for a short time at a temperature just under 1000°C. The operations are carried out in a vacuum and are performed twice before wire of a suitable diameter is obtained. Wire has been rolled to about 0.8 mm diameter. Fine wire is prepared by rolling under iron and afterwards dissolving the iron away with acid.

Gases such as argon and helium are not freely soluble in uranium, but hydrogen dissolves in it to the extent of about

1.6 mg in every 100 g of the metal at 1100°C and 760 cm pressure. This fact has been of practical value in vacuum tube work and for the purification of rare inert gases.

The structure of uranium appears to be quite different from that of any other element. Neodymium is the only other element which shows any resemblance to uranium in crystal structure. Uranium is essentially a pseudo metal, such as gallium or antimony. On the basis of both high electrical resistivity and X-ray spectrography, the uranium structure is not that of a typical metallic substance. This partly explains the unusual valences of the element. X-ray data show that it has a tendency to form four covalent bonds. The only similar element, neodymium, forms hexagonal, close-packed crystals, whereas uranium exhibits a distorted hexagonal, close-packed structure, with an orthorhombic unit cell.

Natural Radioactivity and Transuranic Elements

Freshly prepared uranium emits alpha particles. Uranium of atomic weight 238, after losing an alpha particle (a helium ion of mass 4), degenerates into an element whose mass is 4 units less than that of the original uranium. This process, as is well known, continues despite external physical influences.

Uranium is just one of some 40 natural radioactive elements, practically all of which have atomic numbers between 81 and 92. They are grouped into three series: the uranium-radium series, the thorium series, and the actinium series.

In each of these series, which are made up of many distinct radioactive elements, any one of the members may be traced back to a parent element by transformations which involve the emission of an alpha particle or an electron. In the uranium-radium series, a lead isotope is the end product.[36]

In minerals containing uranium there is always present a small amount of radium. The ratio which exists between these two elements when radioactive disintegration has reached equilibrium is defined by Boltwood's constant. This means

that one part radium is always present for every 3,400,000 parts uranium in minerals which have reached equilibrium. The young minerals, geologically speaking, are an exception, the radium-uranium ratio depending on the age.

Transuranic Elements

Elements heavier than uranium may have existed at one time. The explanation as to why they do not exist at present is probably their comparatively short lives. This means that elements heavier than uranium, called transuranic elements, may have existed once, but they disintegrated rapidly. It means, further, that uranium may be only an intermediate in a now extinct radioactive series. It also means that the radioactive series we know are merely remnants of the series which once may have included a large number of transuranic elements. Among the light elements only three are known which are naturally radioactive. These (potassium, rubidium, and samarium) may also be remnants of a now extinct radioactive family, the other members of which are now gone or have disintegrated into many of the known non-radioactive elements.

Fluorescence and Phosphorescence [37]

Uranium compounds are remarkable in that they fluoresce when dry and apparently when pure, although it has been suggested that the luminescence of uranium compounds is due to isotopic activation from radioelement end-products produced by disintegration. Uranyl compounds and practically all luminescent uranium minerals emit in the yellow and green regions of the spectrum, regardless of the exciting wavelength. Increasing complexity causes shifting of emission into the blue, and less frequently into the red or orange regions. One of the striking things about the fluorescence of the uranyl salts is that a change in temperature of from +20°C to —180°C causes the bands which make up the ordinary fluorescence spectrum of uranium to resolve into narrow line-like bands, with a simul-

taneous increase in intensity and a slight shift in wavelength.

This property has proved very valuable to chemical and physical science, and with it new methods of analysis, microscopy, spectroscopy, prospecting, etc., have come about. It is beyond the scope of this book to include a discussion of the various theoretical and practical aspects of luminescence.

Chemical Properties

Uranium metal is fairly reactive and resembles iron in many of its chemical properties. Powdered uranium reacts slowly with cold water, and more quickly with hot water. It is not perceptibly affected by concentrated alkali solutions, such as potassium hydroxide. Uranium dissolves in mineral acids, liberating hydrogen and forming a uranous salt. It combines with fused sulfur and selenium. With carbon, the carbide, UC, is formed. Uranium displaces mercury, silver, copper, tin, platinum, and gold from their solutions. The reaction of uranium with ammonia gas is accompanied by incandescence; ammonium hydroxide has little effect on the metal.

Compounds

Elemental uranium exhibits four valences: three, four, five, and six, although many misstatements are to be found in the literature regarding the combining capacities of this element. Little has been published about trivalent uranium compounds, three halides being outstanding examples.

Tetravalent uranium is established by the existence of four halides, and a number of other compounds. A number of organo-uranium compounds are known which contain tetravalent uranium. These compounds of tetravalent uranium are termed *uranous* compounds. The basic tetravalent oxide, UO_2, which is found in minerals, is an important representative.

When liquid chlorine acts upon uranium tetrachloride, the pentachloride forms. Varying yields of uranium pentachloride are produced when the metal is chlorinated.[38]

The most stable and important compounds of uranium are those in which the element is hexavalent. Hexavalent uranium compounds, apart from UF_6, are oxygenated and give rise to the important bivalent cation uranyl, UO_2. When uranous compounds are oxidized, uranyl salts form. Uranous compounds are green; uranyl compounds are yellow and have a characteristic yellow-green fluorescence.

The uranates containing hexavalent uranium are regarded as derivatives of metauranic acid, H_2UO_4, the anhydride of which is the acid anhydride, UO_3. The uranates, like tungstates and molybdates, form complexes by the replacement of oxygen by UO_4 or UO_3.

Uranium often occurs in nature in the form of one or more of its oxides. The two chief types, as previously mentioned, are the basic uranous oxide, and the acid anhydride. An intermediate oxide, urano-uranic oxide, U_3O_8, makes up the greater part of pitchblende.

Recovery from the Ore

The important ore-minerals of uranium are pitchblende and carnotite. Uranium is usually obtained as a by-product from the chemical processing of carnotite for its vanadium and/or radium content. Hand-picked concentrates from pitchblende are generally digested with nitric acid or aqua regia after a thorough pre-roasting in a reverberatory furnace to remove arsenic, sulfur, and other volatile elements. Instead of treatment with acid, as was the procedure in early methods for extraction, the roasted ore may be fused with sodium carbonate or sodium sulfate. The uranium is converted to the uranate, together with the formation of molybdates, vanadates, and tungstates. These pass into solution when the cold material is extracted with water. The residue contains radium, which is treated further.

The uranium solution is digested with sulfuric acid, which reacts to form uranyl sulfate. The excess acid is removed by

evaporation and the residue is extracted with water. The residue consists mainly of silicon dioxide, lead sulfate, and basic bismuth sulfate and arsenate. The two extracts are treated with an excess of sodium carbonate to precipitate the basic carbonates of iron, aluminum, nickel, and cobalt. The uranium remains in solution.

The uraniferous solution is boiled, the clear liquid neutralized with dilute sulfuric acid, and then boiled down until sodium diuranate appears as a bright yellow precipitate. The use of ammonium salts instead of sodium compounds in the processing of uranium is often preferred, since ammonium diuranate is obtained, and this can be ignited to U_3O_8.

In order to obtain pure uranyl salts from the above fractions, treatment with nitric acid is employed. The hexahydrate crystallizes out, subsequent crystallizations often being used for additional purification. A fine paper has been written by Kuebel [39] on the extraction of radium from Canadian pitchblende, essential aspects of uranium recovery also being discussed. The accompanying diagram shows how uranium is recovered as a by-product from pitchblende treated by roasting with sodium chloride and then leaching with sulfuric acid (table 25).

Preparation of the Metal

The first isolation of uranium metal was accomplished by Peligot [40] who, in 1842, showed that Klaproth's attempts to isolate the element by reduction with carbon were invalid. Peligot prepared the metal by reducing the chloride with metallic sodium; later Zimmerman substituted potassium chloride for the sodium chloride interposed between the uranium chloride and sodium layers in Peligot's procedure. Electrothermic reduction has yielded elemental uranium.

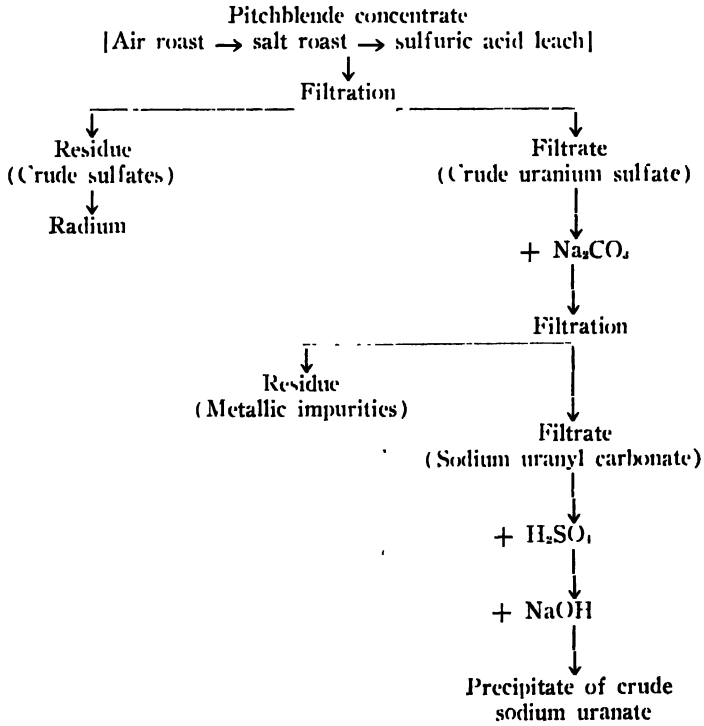
The most recent methods of preparing uranium metal are based on calcium metal or, better still, calcium hydride as the reductant. With the latter reductant the use of steel pressure

bombs is not necessary. The hydrogen as well as the calcium acts as a reductant.

Undoubtedly the most successful technique for preparing large amounts of uranium is the electrolysis of fused salts by the Driggs and Lilliendahl process, developed in 1930.[41] Fused salts, such as those of tetravalent uranium, mixed with alkali

TABLE 25

URANIUM RECOVERY FROM PITCHBLENDE[39]



halides and/or alkaline earth halides, are electrolyzed at fairly low temperatures. A typical bath consists of potassium uranous fluoride in a mixture of equal parts calcium chloride and sodium chloride. A loosely adhering deposit of metallic uranium is obtained on the cathode.

Technology

Although on the whole uranium has not found the wide applications of the other metals of its family, certain unusual properties of the element have resulted in enormous advances in our civilization. It was due to uranium that the science of radioactivity, the discovery of radium, the verification of the existence of helium on the earth, and the remarkable successes of radiation in medical therapeutics have all come about. It is believed that uranium may be the fuel of the future. At present, there is a growing interest in uranium because of the knowledge about fluorescence gained through a study of its compounds.*

Metallurgy of Uranium

Uranium readily alloys with other metals. It has been alloyed with copper, zinc, magnesium, mercury, aluminum, titanium, vanadium, molybdenum, tungsten, manganese, iron, cobalt, and others. Usually the alloys are prepared by aluminothermic reduction.

A few alloys of greater complexity have been prepared, such as a ternary alloy of uranium, iron, and manganese. A quaternary alloy consisting of uranium, molybdenum, titanium, and chromium has also been produced. The carbide and intermetallic compounds of uranium with antimony and arsenic are known.

A new binary alloy of uranium and nickel, containing 66 per cent uranium, is useful in that it is very resistant to corrosion, and is attacked with difficulty by aqua regia. This alloy has a low melting point and is quite miscible with molten steel, nickel, and copper.

An alloy of uranium and copper has been prepared, containing up to 20 per cent uranium. Its desirable properties include high conductivity and resistance to corrosion. An assured sup-

* The beginnings of precise knowledge about the fluorochemistry of uranium salts dates back to 1853, to the time of Sir G. G. Stokes.[42]

ply of uranium would lead to important outlets in the metallurgical field.

Uranium alloys added in small amounts produce desirable physical properties in tool steels. The uranium-nickel alloy or ferrouranium, the more readily available source of this metal, may be employed for commercial applications. Stainless silverware can be made by plating the ware in an electrolytic bath containing silver fluoride and compounds of uranium and tin.[13]

As a research tool, uranium has been a useful source of strong monochromatic X-rays. Slack has studied the properties of uranium for anticathodes in X-ray tubes. The X-ray efficiency of uranium, as compared with other important target metals is as follows: U:Th:W = 125:120:91.

The wavelengths emitted from uranium targets are of course different than those obtained from either tungsten or thorium (see chapter 3, table 12).

Uranium in the finely divided state is pyrophoric. When prepared properly the gray or black powder unites vigorously with the oxygen in the air to form an oxide. Pyrophoric uranium may be obtained by reduction of the oxide with magnesium in the Goldschmidt reaction. Finely divided alloys of iron and uranium containing more than 20 per cent uranium are pyrophoric, and it appears that the activity increases with the uranium content of this binary. Uranium carbide, UC, will emit a shower of sparks when filed.

Uranium Fission—Atomic Power [34]

The importance of uranium has been greatly enhanced by its relation to radium. But of still greater promise is the use of uranium in an entirely new role, *nuclear fission.*

Shortly after the discovery of the neutron by Chadwick, after its prediction by Rutherford, and the discovery of artificial radioactivity by M. and Mme. Joliot-Curie in 1934, Fermi and his co-workers (1934) demonstrated that heavy elements

such as uranium and thorium are capable of capturing neutrons, thereby becoming highly radioactive.

This activity was found not to be associated with the transmutation of the target element into any of the elements between lead, with an atomic number of 82, and uranium, with an atomic number of 92. Fermi and his co-workers reached the startling conclusion that transuranic elements, those with atomic numbers 93, 94, and so on, had been synthesized. This interpretation was generally held to be correct until January, 1939, when Hahn and Strassman demonstrated the presence of elements of about half the atomic weight of uranium among the products of such bombardments. These observations of the *fission* of the heaviest elements were confirmed almost immediately.

Accordingly, the existence of Fermi's transuranic elements was open to serious question. On June 7, 1940, however, McMillan of the University of California, and Abelson of the Carnegie Institution of Washington, announced that elements 93 and 94 actually could be synthesized. Instead of having properties which would characterize eka-rhenium and eka-osmium, the new elements appeared to correspond more closely to uranium, suggesting the existence of a new series of elements analogous, but chemically dissimilar to, the rare earths (atomic numbers 57 to 71). This new series makes its appearance with element 93 as the first member. The series of transformation reactions is:

$$_{92}U^{238} + {}_{0}n^{1} \longrightarrow {}_{92}U^{239} \xrightarrow{\text{23 minutes}} \underset{\text{(Neptunium)}}{[93]^{239}} + \beta$$

$$[93]^{239} \xrightarrow{\text{2.3 days}} \underset{\text{(Plutonium)}}{[94]^{239}} + \beta$$

No alpha or beta ray activity or evidence of nuclear fission was detected which could be associated with the decay of $[94]^{239}$. This transuranic element, called plutonium, is quite

long lived, though it has since been shown to be radioactive.

Even more striking is the explanation of the origin of the elements of low atomic weight. It was noted that two atomic products of fission were ejected in opposite directions at extremely high velocities, carrying enormous quantities of energy. Because of their low kinetic energies, particles of $_{92}U^{239}$ and $[93]^{239}$ remain in the layers of target material, but the products of fission escape with such violence that they may be caught a few centimeters from the target and examined chemically. The energies are of the magnitude of 200 Mev or 4.6×10^{12} calories per gram-atomic weight of uranium. It is this tremendous quantity of energy that has given hope that nuclear fission may be a useful source of power. The energies released in the fission of one uranium atom are fully 40,000,000 times greater than those released by one molecule of T.N.T. in exploding.

In April, 1940, Nier, of the University of Minnesota, and Booth, Dunning and Grosse, of Columbia University, announced that sub-microscopic quantities of the natural isotopes of uranium, i.e., U 234, U 235, and U 238, had been separated by means of the mass spectrograph and individually subjected to neutron bombardment.

It was found that only uranium 235 undergoes fission under the action of slow neutrons; uranium of mass 238 is also capable of absorbing slow neutrons, but is transmuted into element $[93]^{239}$, just as with more energetic neutrons. The exact sequence of events after the capture of a slow neutron by $_{92}U^{235}$ is still not known with certainty, but fission is accompanied by the escape of many more fast neutrons than are captured, which makes possible the initiating of a chain reaction. This can occur only in the presence of non-absorbing objects, such as water, which reduce the kinetic energy of the secondary neutrons to thermal equilibrium values.

The complex particle formed by the capture of a thermal neutron by $_{92}U^{235}$ bursts in 10^{-12} sec into at least two groups of

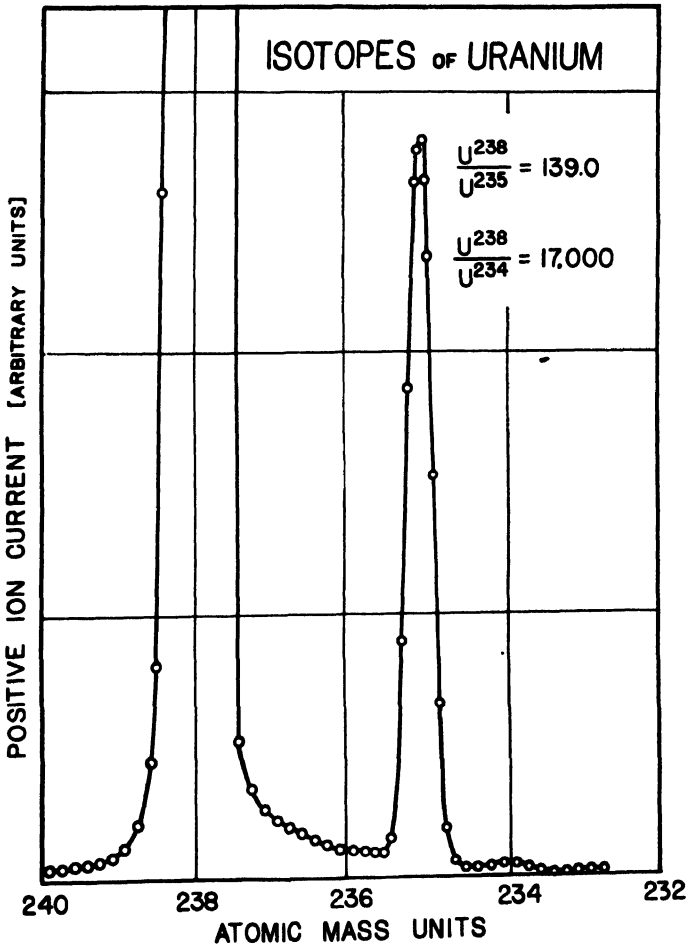


FIGURE 28

Mass spectrum showing the relative abundance of the uranium isotopes (courtesy of Dr. A. O. C. Nier, University of Minnesota).

The points for the curve are obtained by plotting positive ion current passing through the exit slit of the analyzer, as a function of the energy of the ions in a constant magnetic field. A definite relation exists between the energy and the mass of the ions collected. The width of the peaks is due to focusing imperfections and the finite width of the slits used.

atomic particles, the nature of which remains uncertain because of their short half-lives. The process of fission is highly complex. In addition to the fast neutrons ejected, two groups of isotopes are formed in the disintegrations of atomic species resulting from fission. The two classes of elements are known as the heavy group and the light group. In the heavy group, atomic weights range between 80 and 100. A reaction has been given by Grosse to explain fission (see table 26).

If the atomic weights of individual isotopes are unknown the element is characterized, in the equation, by the half-life of its parent. The equation shows that, for the fission of every 100 uranium 235 atoms, there will be produced 100 atoms of the heavy group, and at the same time 100 atoms of the light group. In addition to these and neutrons, enormous quantities of energy are emitted. Among the other elements which have been detected in the disintegration of atomic species resulting from fission are: $_{35}$Br, $_{36}$K, $_{37}$Rb, $_{38}$Sr, $_{39}$Y, $_{40}$Zr, $_{41}$Cb, $_{43}$Ma, $_{51}$Sb, $_{52}$Te, and $_{56}$Ba.

TABLE 26

FISSION OF URANIUM 235

$$100_{92}U^{235} + 100_{0}n^{1} \longrightarrow$$

$$6.1_{42}Mo^{(ex\ 75\ m.\ Cb)} + \ldots \text{ [Light Group Elements]}$$

Heavy Group Elements

$$0.18_{53}I^{127} + \ldots$$

$$0.34_{54}Xe^{129} + 1.6_{54}Xe + 5.2_{54}Xe^{(ex\ 2.4\ hr.I)} + 12_{54}Xe^{(ex\ 54\ m.I)} + \ldots$$

$$7.6_{55}Cs^{133} + 9_{55}Cs^{135?} + \ldots$$

$$6.4_{57}La^{139} + \ldots$$

$$8.4_{58}Ce^{140(ex\ 40\ hr.La)} + \ldots\ldots\ldots\ldots\ldots\ldots$$

Other Uses of Uranium

In 1934 Marden studied uranium from a standpoint of its use in gas discharge devices. The use of uranium in commercial gas discharge devices is a matter of considerable importance. The potential required to initiate a discharge between two

electrodes in a gas is dependent upon the distance between the electrodes, the material, the surface condition of the electrodes, and the nature, purity, and pressure of the gas.

Uranium is so reactive with ordinary gases, such as oxygen and nitrogen, that these gases are rapidly consumed when a discharge is initiated between electrodes of uranium. If impure inert gases are employed, the electrodes serve to purify the gas. Impurities liberated from the walls of the bulb or other parts of the discharge device are also cleaned up, and high gas purity results.

The breakdown potential of devices using uranium therefore remains remarkably constant so long as the discharge current is not high enough to drive the inert gas into the electrodes, thus changing the gas pressure. Glow rectifiers and low voltage regulator tubes have been constructed with uranium electrodes which showed practically the same discharge characteristics over a period of 20,000 hours of continuous operation.

The compounds of uranium of chief interest to the glaze maker are the oxides. Probably the most important is U_3O_8, the green oxide of uranium. The black oxide of uranium, UO_2, is also used for this purpose. Other compounds which are used by the ceramist are sodium diuranate ($Na_2U_2O_7$) (*uranium yellow*), ammonium uranate (also known as *uranium yellow*) and the hydrated sodium uranate ($Na_2U_2O_7.6H_2O$) (also called *uranium yellow*). Potassium diuranate, $K_2U_2O_7$, is called *uranium orange*.

In Germany, a hydrated sodium uranate (*urangelb*) is available for use as a coloring agent in glasses. It differs from the first sodium uranate in that it has three water molecules less. In addition to oxides, other compounds such as the double salt, sodium uranyl carbonate, and the nitrate and sulfate, have been suggested.

Related to its use as a colorant in ceramics is the use of uranium for coloring glass. The element is not a powerful colorant, as compared with elements such as chromium or

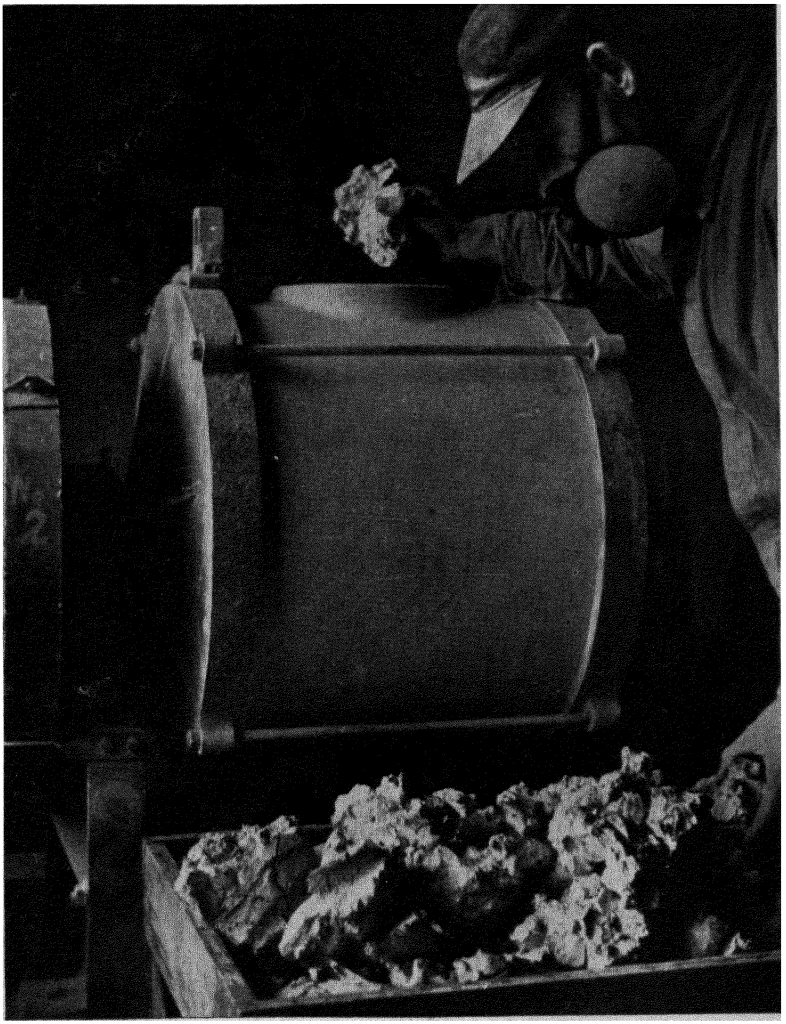


FIGURE 29

Grinding sodium uranate in a porcelain-lined ball mill.

Contact with metal should be avoided during grinding as even very minute amounts of metal can affect its qualities as a pigment for glass and ceramics.

cobalt, but deep colors may be obtained when larger proportions of the substance are incorporated in the batch of glass. The uranium glasses are unique since they are highly fluorescent in ultraviolet radiations of all wavelengths as well as in white light. The fluorescence is so intense in bright white light that the glass appears to be self-luminous.

Analysis

Uranometry is the term applied to the detection and determination of uranium. The two extremes in uranometry are illustrated by the researcher with his intricate techniques involving equipment such as the mass-spectrograph, and the prospector hand-examining a specimen believed to be uranium- and radium-bearing, judgment being based on simple properties like color, specific gravity, hardness, luster, and feel.

A great many methods have been developed for the detection and determination of uranium. In a recent treatise on uranium, the following approaches to uranometry are discussed in detail: [34]

1. Gravimetry
2. Volumetry
3. Electrolytic procedure
4. Colorimetry and nephelometry
5. Electroscopic and counter methods
6. Spot tests and organic precipitants
7. Spectrochemical analysis
8. X-Ray spectroscopy
9. Fluorochemical analysis
10. Microchemical methods
11. Radiographic tests
12. Microscopic determinations
13. Polarographic analysis
14. Chromatographic and capillary analysis
15. Fire assay
16. Radiochemical analysis

It is evident how complex the analytical chemistry of uranium is. Uranium is radioactive, usually being contaminated with other radioelements; uranium forms compounds which are among the brightest fluorescing substances known; the multi-valency leads to many complications in its analysis and even detection, when the usual chemical methods are employed.

Scholl's Rapid Method

A rapid and accurate method for the determination of uranium was developed in 1919 by Scholl.[45] It is called the Rapid Method. In it the uranium is extracted from its ore with a dilute nitric acid solution (1:1), diluted, and filtered. Ferric chloride and sodium carbonate are then added to precipitate the vanadium and iron and a greater part of the aluminum. The uranium is precipitated from the filtrate by boiling with sodium hydroxide and purified by dissolving in nitric acid. It is then precipitated by ammonium hydroxide as ammonium uranate, ignited to U_3O_8, and weighed.

One of the simpler methods for the estimation of uranium, especially when in comparatively pure solutions, is the precipitation of the uranate by ammonium hydroxide, and the isolation and ignition of this precipitate. This procedure was described in 1904 by Kern.[46]

In 1928 Fenner investigated the methods of uranium analysis for their value in age calculations. Fenner pointed out that there is considerable literature on the subject, but not much that is well systematized, nor formulated to meet the special requirement demanded in age determinations. Moreover, some of the methods appear to be applicable only under certain conditions, but their limitations are not stated. While many methods are of a high order of accuracy, others lead to results which appear improbable. Analytical accuracy is one of the most fundamental of the factors entering into the calculation of geologic age.

In Fenner's method for the determination of uranium and

thorium in euxenite, polycrase, samarskite, and others, only 2 or 3 g of the powdered sample are required. To this five times as much sodium bisulfate is added and the mixture fused at bright red heat until the evolution of sulfuric anhydride nearly ceases. The product of fusion is cooled and sulfuric acid is added. The mixture is digested for 1½ hours while exposed to the fumes of sulfuric anhydride. The material is cooled, dissolved in cold water and allowed to stand overnight.

Uranyl ferrocyanide is the brown compound salt produced when soluble ferrocyanides, e.g., the potassium salt, are added to solutions containing uranyl ions. Copper forms a similar brown precipitate with ferrocyanides, but the two may be differentiated by the addition of potassium hydroxide solution, resulting in a yellow coloration from the formation of the uranate. The solubility of uranyl ferrocyanide, as differentiated from the solubility of the copper salt, is another factor which identifies them. In actual test the solution to be examined is acidified with hydrochloric acid and a small amount of sodium chloride is added to prevent colloidal precipitation.

Electrical Methods

Electroscope and counter detection of uranium have a number of advantages not possessed by most of the other procedures. Radium, a powerful radioelement, is always associated with uranium in nature. By the presence of radium the detection and determination of uranium is performed with greater ease, since both emit ionizing radiations by which their existence in a specimen may be verified. It will be noted, however, that thorium may cause the discharge of an electroscope or Geiger-Muller counter.

The determination of the amount of uranium is based on the time required for the charged leaf of an electroscope to pass a certain number of graduations on a scale. A sample of uniformly ground ore of a definite surface area and weight is placed at a fixed distance from the conducting plate of the

system, and its activity noted. Finally, the analyzed sample is determined in the same way. Aside from the deduction of the natural leak of the instrument, the two activities may be directly compared and the amount of uranium determined in the unknown in terms of the known, a small variation being allowed for error.

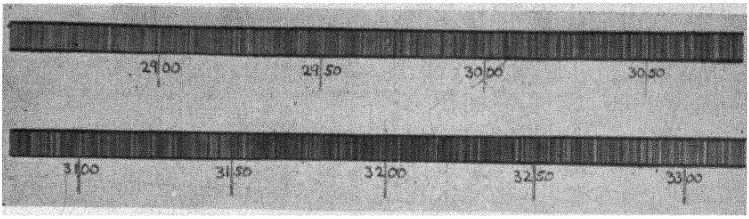


FIGURE 30

Portion of the ultraviolet spectrum of uranium (courtesy of Dr. W. F. Meggers, National Bureau of Standards).

Only about 5 per cent of the entire range that can be recorded photographically is illustrated. This is typical of the whole, which consists of many thousands of fine lines, demonstrating the impracticability of direct spectrochemical analysis of uranium.

Fluorochemical Analysis

All uranium minerals are potentially fluorescent.[48] This fluorescence is best evoked by short wavelength ultraviolet radiations, e.g., those supplied by the Mineralight lamp.* Solutions of uranyl salts are also fluorescent, and the solids show the property to a marked extent. With rare exception, the fluorescence of uranium minerals and solutions is a characteristic green, yellow, yellow-green, or yellow-blue in color. Dispersed in silica, concentrations of uranium far below the limits of ordinary chemical tests show their presence by a bright fluorescence. The yellow fluorescence of certain Wyoming and Nevada opaline silicas is due to traces of uranium.

* The Mineralight can be secured from the Ultra-violet Products, Inc., 5205 Santa Monica Blvd., Los Angeles 27, Calif.

The portable cold-quartz Mineralights are especially useful for field work, since they provide the 2537Å ultraviolet light that gives the best response.

The primary uraninites (pitchblende) and the columbium-titanium-tantalates are generally non-fluorescent, but the secondary uranium minerals are often brilliantly fluorescent. Since the secondary minerals are often associated with the primary ones, their fluorescence may indicate an outcropping of a larger, more valuable body of a primary ore. An illustration is zippeite, a secondary mineral found on outcroppings of pitchblende. Its existence is due to weathering of the original mineral. Zippeite fluoresces with a medium strong yellowish color under short wavelength ultraviolet radiation.

De Ment and Dake [15] cite the 1940 investigations of Miexner on the fluorescence of uranium minerals. Miexner classified the uranium minerals into three classes: (a) strongly luminescent, (b) weakly luminescent and (c) non-luminescent, according to their response under ultraviolet light. These investigations qualify the fact that primary uranium minerals are usually not fluorescent, while the secondary ones often are.

The strongly fluorescent uranium minerals are the uranium phosphates, arsenates, sulfates and others which fluoresce with a strong yellow-green color. The uranium carbonates fluoresce a greenish color. The non-luminiescent uranium minerals include the silicates and uranium micas of the following composition:

$$M_2(UO_2)_2(XO_4).nH_2O$$

where M may be copper, iron, lead, bismuth, manganese or uranium dioxide, X may be phosphorus, arsenic, vanadium, or sulfur, and n from 8 to 12.

The non-fluorescent uranium minerals usually have a drab color, often being black or brown. The fluorescent secondary minerals are usually lighter in color, sometimes being light

yellow. They generally have a specific gravity about half that of the pitchblendes. Table 27 lists the fluorescent responses of uranium minerals under ultraviolet light. These color values are seen regardless of the locality.

TABLE 27

FLUORESCENT URANIUM MINERALS

I Strongly Fluorescent

Autunite	Yellow-green
Beta-uranopilite	Yellow-green
Chalcolite (cf. torbernite)	Yellow-green
Johannite (variable)	Yellow-green
Metatorbernite	Yellowish-blue
Schoepite	Green-yellow
Schroeckingerite (Dakeite)	Green
Torbernite	Yellow-green
Uranocircite	Yellow-green
Uraniferous hyalite	Yellow-green
Uranophane	Yellow-green
Uranopilite	Yellow-green
Uranospathite	Yellow-green
Uranospinite	Yellow-green
Uranothallite	Green

II Moderately Fluorescent

Gummite (variable)	Violet
Beta-uranotil	Yellowish
Uranotil	Yellowish
Zippeite	Yellowish

In prospecting for uranium minerals without chemical tests, it is recommended that known specimens be examined with the lamp before appraisal of an unknown sample is attempted.

Failure to note fluorescent uranium minerals in the field may not mean the absence of pitchblende or carnotite, as indicated previously. It is strongly advised that chemical tests, which are easily employed in the field, be relied upon for the final qualitative test. Several fluorochemical tests for uranium can also be used.

When dissolved in water, and in the absence of certain interfering elements, the oxygenated uranium compounds, i.e., those containing the so-called *uranyl* (UO_2) group,[34] fluoresce brightly under ultraviolet light. This glow is better seen with the radiations released by a short wavelength lamp than by the units which generate the long wavelength ultraviolet rays. This is equally true of traces of uranium dissolved or disseminated in a solid base material like silica or some chemical compound like sodium fluoride.

The primary uranium ores are generally those to which attention is directed in qualitative tests, since they cannot be distinguished under the lamp without preliminary treatment.

All uranium ores are attacked by aqua regia or by nitric acid. In the simple tests a solution may be secured by boiling a few grams of the sample in 10 cc of aqua regia or nitric acid.

The following fluorochemical methods of testing have been found to be extremely sensitive for detecting uranium. They are presented here for those who wish to employ them in the field or in the laboratory in connection with the ultraviolet lamp. The method selected will depend upon the operator and the conditions under which he works.

Bead Tests

The bead test comprises the fusion, on the tip of a platinum wire with a loop in the end, of an inorganic salt like borax or calcium fluoride with a small amount of the unknown. The bead may be formed in the flame and then dipped into a solution of the unknown, re-fused, re-dipped, re-fused, and so on, until a fairly large bead is obtained.

Sodium, potassium, or calcium fluoride is the best bead material for uranium tests. A pure, non-fluorescent fluorite can also be used. Borax proves satisfactory. While fine particles of the mineral sample can be fused directly into the bead, it is best to dip the bead into a solution of the sample during the test. When the bead is completely formed and after it has cooled, it is

examined under the lamp. If uranium is present, the bead will fluoresce a bright green, yellow-green or lemon-yellow color. The sensitivity of bead tests, when ultraviolet inspection is used, is great, as little as 1 molecule of uranium compound in 10,000,000 molecules of bead material causing the fluorescence. This corresponds to far less than 10^{-6} of uranium.

Before using the bead test, pure uranium compounds and samples of pitchblende or carnotite should be used to make up standards for comparison. The bead test may be used quantitatively, but special equipment and standardized working conditions are required.

The Zinc Test

The writer [49] has developed a simple test for uranium which can be used in conjunction with the ultraviolet lamp. All that is required is a lamp, a small bottle of aqua regia (a mixture of 1 part nitric acid and 3 parts hydrochloric acid) and a box of granular zinc of good purity. The procedure is to heat 5 g of the finely ground mineral sample in 20 cc of aqua regia for several minutes, complete solution not being required. This liquid is diluted with 80 ml of water, and several lumps of granular zinc added. The preparation is then allowed to stand for up to ½ hour, and the lumps of zinc removed before they dissolve.

The lumps of zinc are then gently flamed over a bunsen burner until a pale yellowish coating begins to form on the surface. At this stage the zinc is allowed to cool and inspected under ultraviolet light. In the presence of uranium, bright yellow or green fluorescent spots will be observed over the zinc. If the results are negative, the lump of metal is further heated and, after cooling, re-examined. The uranium spots may also have a short afterglow.

Care should be taken not to over-heat the zinc, since it fuses rather easily in the flame, although at temperatures of incipient fusion the coating on the zinc will show several color changes

—from pale yellow, through deep yellow, orange, orange-red, and finally ending in a dark brownish deposition. These color successions will be seen when the sample contains uranium.

The zinc test is very sensitive, responding to carnotites containing less than 2 per cent uranium oxide. With the amount of material dissolved from pitchblende by the means mentioned above, it will also give positive results. However, tests should be conducted with uranium salts and known samples before attempting to use it on an unknown. It is convenient to save the lumps of zinc which do show uranium for comparison in subsequent tests. In certain cases the fluorescent specks will appear as bluish hues of yellow or green. These may be taken as positive, but bright blue areas, which are due to reflections on a shiny metal surface, should be disregarded. With a little practice, the zinc test will yield reliable results.

Bureau of Mines Test

Sill and Peterson,[50] working at the U. S. Bureau of Mines Experiment Station in Salt Lake City, Utah, have developed a simple but reliable fluorescence test for uranium using the short wave ultraviolet lamp. They state that the available methods for detecting uranium have lacked one or more of the desired characteristics, and that this method is probably more specific and sensitive than the usual qualitative methods for uranium. Its speed of application and simplicity make it ideal for testing samples prior to quantitative analysis.

The fluorescence test has been tried for over 2 years by these workers on various types of uranium minerals with very reliable results. Samples submitted for uranium analysis can be tested at the outset for uranium. Those containing uranium can be subjected to the more complicated and accurate quantitative tests, but those containing no uranium can be eliminated, thereby effecting a large saving in time and expense. The test has the advantage of using up none of the sample; it is an integral part of the quantitative scheme of analysis, so if

uranium is found, the analyst can continue with the quantitative determination.

Sill and Peterson took advantage of the observation of De Ment and Dake [31] that aqueous solutions of uranium are much more responsive to short wavelength ultraviolet light than to long wavelengths. Their test readily detects as little as 0.3 mg of uranium at a dilution of 1:1,000,000 but if smaller volumes of uranium extract are inspected, the delicacy of the test is increased greatly.

Procedure

Weigh 3 g of the ore into a 400 cc beaker, and dissolve with hydrochloric, nitric or hydrofluoric acids, as required. The solution of the specimen is achieved in the same way as in the zinc test described above. To this, 15 cc of sulfuric acid are added, and the mixture heated until fumes of sulfur trioxide appear. Any dark coloration due to organic material should be removed by the dropwise addition of perchloric acid to the fuming solution. Most of the sulfuric acid is then removed by fuming, and the liquid allowed to cool. It is diluted with water to 100 cc, and heated until all soluble salts are in solution. It is then filtered, using paper pulp if necessary to give a clear filtrate, and diluted to 150 to 200 cc.

UV Examination: It is recommended that only the short wavelength light be employed in inspecting the liquid, since the long wave unit does not provide satisfactory results. The fluorescence test is conducted in a dark room, and the eyes of the operator should be protected with plain, colorless glasses if the inspection is to go on for a period of 15 minutes or more. Pyrex beakers, of 400 cc capacity, are chosen for their low fluorescence, and the solutions are placed in these.

The clear solution is placed on a black, non-reflecting surface, like velvet, and the ultraviolet lamp is placed on the open top of the beaker.

In the presence of uranium the fluorescence will usually be

seen as a bright greenish-yellow line immediately below the meniscus, if the eyes are at the same level as the meniscus and the solution viewed at right angles to the incident beam. If the eyes are lower, the entire under-surface of the solution glows greenish-yellow. This line, though narrow, stands out in strong contrast to the rest of the solution. Such a line is seen when foreign substances are present which absorb the ultraviolet light, but in solutions that contain no absorbing substances the fluorescence is distributed throughout the solution. It may be more greenish than the line described above. With increases in uranium content, the volume fluorescence tends to disappear. This phenomenon not only involves absorption, but also the principle of *concentration quenching*.

Since certain substances interfere with the uranium fluorescence, the following corroborating test should always be applied to establish the presence or absence of uranium. Test the solution as described. If no fluorescence is seen, uranium is not present, provided no inhibiting agent is present. Then add about 0.025 N uranyl sulfate solution dropwise to the solution under test, stirring the solution, and examining under the lamp after the addition of each few drops. If the fluorescence shows up after the addition of a few drops, the conditions for fluorescence were favorable, and since no fluorescence was originally observed, it is fairly certain that the original uranium content was not greater than the amount added.

Should the fluorescence fail to appear after several drops have been added, or if it should appear only very faintly after the addition of a fairly large amount of uranium solution, it may be assumed either that some inhibiting agent is present or that the ultraviolet light is being absorbed too completely. The appropriate separations must then be made to eliminate this difficulty before the test can be applied successfully.

On the usual ores, such difficulties are rarely encountered, since the method of preparing the sample eliminates most of the interfering substances. Samples containing large amounts

of iron may offer some difficulty, especially if large samples are taken to detect small amounts of uranium, owing to a quenching (or dimming) and absorbing action. In any event the presence of any interference will be noticed if this test is used, and the analyst can then take the proper steps to eliminate the difficulty.

The above test also gives a measure of the sensitivity of the test on each particular sample, since it may vary, depending upon the kind and amounts of other elements present. In the usual type of low-grade uranium-vanadium ore (e.g., carnotite), 2 to 3 drops of 0.025 N uranyl sulfate solution in 200 cc of solution can easily be seen. This would indicate a sensitivity of about 0.3 mg of uranium at a dilution of 1:1,000,000. However, by reducing the 200 cc volume, a much smaller amount of the element can be detected.

De Ment recommends that after the Sill-Peterson test has been applied, both the bead test and the zinc test be used on the solution. This corroboration will make the presence of uranium practically certain, and both corroborating tests are simple and quick to use.

Interfering Elements: There are several ions that inhibit the fluorescence of uranium solutions and at certain concentrations may completely destroy it. Highly colored elements may obscure the fluorescent line. If continued runs on many samples are made, it is advised that reference be made to the original report of Sill and Peterson [50] regarding the elimination of these substances.

This test has also been used on columbium-tantalum ores, but the sample must be decomposed by pyrosulfate fusion and leaching with dilute sulfuric acid. It has been most helpful in checking separations employed in the conventional quantitative schemes of analysis. Other applications have been found in studying the amount of uranium occluded by iron hydroxide and the retention of uranyl ammonium phosphate (a substance formed in the conventional wet methods) in the pores of filter paper.

Uranium Mineral Guide

In 1940 De Ment outlined a tentative guide to be used in prospecting for radium and uranium minerals. This can be adapted to prospecting for uranium by means of fluorescence, and the eight points should be kept in mind when using the lamp. A general summary and guide of the fluorescence characteristics of uranium minerals follows:

I. Primary uraninites (pitchblende) do not fluoresce.
II. A number of secondary uranium-bearing minerals are highly fluorescent, i.e., those which contain the uranyl group. In chemical tests which alter primary minerals, substances are produced which resemble the secondary minerals.
III. In practically every case of fluorescence the characteristic yellow-green, or a hue of yellow-green, is observed.
IV. Generally, the more soluble uraniferous minerals are those which are fluorescent.
V. The largest number of fluorescent uranium minerals are those which have a specific gravity of approximately 3.5. Few with a high specific gravity fluoresce.
VI. Fluorescence is best excited by short wavelength ultraviolet radiation, e.g., light from the Mineralight wavelengths of 2537Å.
VII. Primary uraninites after weathering frequently alter to secondary and fluorescent species. In this way a dual detection may be made with the lamp.
VIII. The presence of uranium invariably presupposes the presence of radium.

Other Methods for Uranium Analysis[34]

Turmeric is a reagent which may be used for the detection of uranium. Fresh turmeric paper turns an orange-brown color in the presence of uranyl ions. On spotting turmeric paper,

after the brown coloration has been produced, with sodium carbonate solution, a violet-black color develops. The original yellow color of turmeric may be restored by treatment with hydrochloric acid.

Several good microchemical methods have been proposed and used for the detection of uranium, but with the recent introduction of advanced methods of fluorochemical analysis these have lost some favor. Microchemical detection of uranium is usually accomplished by sodium acetate and zinc acetate. The test solution is prepared by mixing dilute acetic acid, sodium acetate, and zinc acetate. These are placed on a slide and evaporated to dryness so that a thin even film is formed.

A drop of solution containing the material to be tested is placed on the slide and acidified with acetic acid. The drop is then drawn in a narrow streak across the dried film. A positive reaction is denoted by the formation of tetrahedra of sodium uranyl acetate. These may also be encountered as octahedra-like monoclinic, polysynthetic twins of sodium zinc uranyl acetate, $NaZn(UO_2)_3.(C_2H_3O_2)_9 + 9H_2O$.

Fluorescence microscopy greatly assists in identifying small crystals of sodium zinc uranyl acetate.

From an analytical standpoint, it is fortunate that a peracid of uranium exists. The peracid group, —O—OH, has a specific action which leads to important applications for the detection of traces of several metals (see Chapter 4, table 16).

Quinaldic acid is a useful reagent for the estimation of uranium. The quinaldic acid is dissolved in sodium hydroxide or ammonium hydroxide, forming, on addition of uranyl salts, a golden precipitate which is insoluble in acids.

Alizarin-S (sodium alizarin sulfonate) forms a deep violet precipitate with uranyl salts. A good discussion of the use of various methods for uranium analysis has been given by Moore.[47] It stresses the ore-minerals of this element and the troubles which are often encountered in accurate chemical work

upon them. Elements other than uranium are also discussed in detail.

Volumetrically, uranium can be determined, using a Jones reductor with zinc as reducing agent. A silver reductor in place of the zinc may be employed. The precision is remarkably good.

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CHAPTER VI

SELENIUM AND TELLURIUM

SELENIUM

History

Many of the fundamental discoveries of chemistry were due to the scientific insight of the noted Swedish chemist, Berzelius.* Because of the keen observations of this investigator, selenium was discovered. In 1817 Berzelius was studying the flue dust from the lead chambers of the sulfuric acid works at Gripsholm, Sweden, where sulfur, obtained from roasting iron pyrites from Fahlun, was employed in manufacturing sulfuric acid. Berzelius found that when the dust was heated, a pungent odor resembling that of "decayed radishes or cabbage" was given off. In the day of Berzelius, investigators considered this odor to be characteristic of tellurium, an element discovered some time previously. However, a more careful study showed that it was due to the presence of an unknown element with the properties of both sulfur and tellurium.

The new element was named selenium by Berzelius, from the Greek word meaning *moon*. The reason for this choice was that the properties of selenium strikingly resemble those of tellurium, whose name is derived from *tellus*, the Latin word for earth. Since the earth and moon are closely related, Berzelius chose the name selenium for his element.

Mineralogy

Selenium is closely allied to sulfur, with which it is commonly associated in nature. It is found native, like sulfur,

*Berzelius discovered the important elements selenium, silicon, thorium, cerium and zirconium.

and also in the selenides of copper, silver, lead, mercury, bismuth and thallium. A few selenides exist as secondary minerals. Although selenium is distributed widely in the earth's crust, it is rarely concentrated in deposits of sufficient richness to enable commercial exploitation for the selenium alone. Hence, the selenium of commerce is obtained as a by-product of the extraction and refining of various metals, chiefly copper.

Authorities agreed that there is more selenium than platinum in the igneous rocks, but the amount is only about that of silver, (see Appendix III). About 25 minerals contain selenium in varying percentages, but none of the species is considered a commercial source. The carnotite ores of Colorado and Utah are potential sources of selenium, as they generally contain about 0.25 per cent selenium. Canadian nickel sulfide is also an important source of selenium; it is a minor constituent of the Sudbury nickel ores.

Selensulfur (volcanite) contains sulfur and selenium, but the percentage of selenium is usually small. Senelsulfur occurs in the lavas of many active volcanos and abounds in certain fumaroles. Some of the rare sulfo salts of silver, lead, and bismuth contain selenium, but these are generally of interest only from a mineralogical standpoint.

The chief source of selenium at present is man-made, the anode mud from the electrolytic refining of copper. Silver, gold, platinum metals, selenium, tellurium and other elements are recovered from the mud. As a rule none of these metals is present in large amounts in the unrefined copper, but as large tonnages are refined, they accumulate in slimes and flue dust and are recovered in considerable quantities.

The selenium in the anode mud is separated by drying and roasting the mud. During roasting the selenium volatalizes off as the dioxide. It is dissolved in hydrochloric acid and reduced with sulfur dioxide in order to obtain elemental selenium. As would be expected, there are a number of selenium minerals which are analogous to those of sulfur. This can be seen in table 28.

TABLE 28

SELENIUM MINERALS

Mineral	*Composition*
Berzelianite	Cu_2Se
Clausthalite	PbSe
Guanajuatite	Bi_2Se_3
Joseite	$Bi_4Te(S,Se)$
Naumannite	$(Ag_2Pb)Se$
Platynite	$PbS.Bi_2Se_3$

Physical Properties

Selenium resembles sulfur in many of its physical properties, forming several allotropes. The specific gravity varies according to the form, ranging between 4.3 and 4.8. The ordinary allotrope is a grayish solid with a semi-metallic luster, which is best seen on a freshly fractured surface. This stable form is crystalline and has a specific gravity of 4.47. It is insoluble in water and in carbon disulfide. It turns black when heated. A closely related allotrope is red and has similar characteristics. Orange allotropes are also known to be crystalline.

Amorphous selenium is a dark red to black powder which softens at 60°C and has a specific gravity of 4.3. It is insoluble in water, but dissolves in benzene and carbon disulfide. A gray "metallic" allotrope, different from the first allotrope described, is lustrous and obtainable in metal-like granules or sticks. It has a specific gravity of 4.8 and is insoluble in water, alcohol, and carbon disulfide but dissolves in ether. A dark red powder, known as the colloidal form, is red and fluoresces in water. On aging, allotropic modification occurs.

Selenium has an atomic weight of 78.96. It has six natural stable isotopes which, arranged in order of abundance, have the following mass numbers: 80, 78, 76, 82, 77, and 74. Artificial isotopes of selenium have been prepared by nuclear reactions.

Selenium melts at 217°C and boils at 690°C, giving off dark red vapors. In a high vacuum it boils at about 310°C. It can

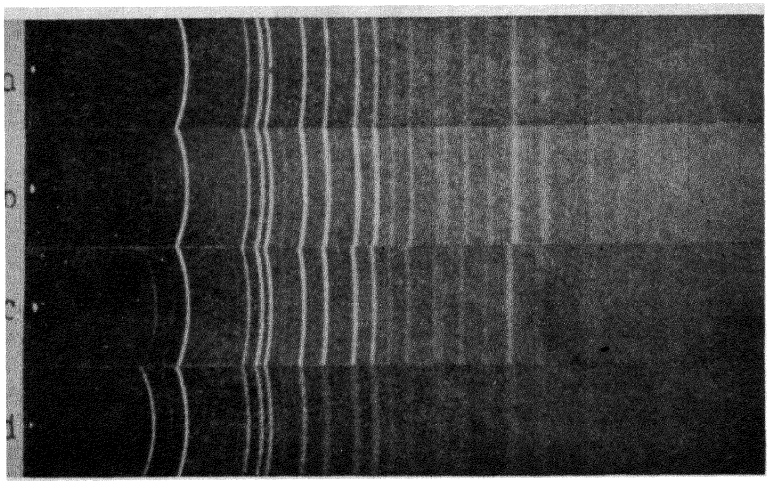

FIGURE 31

X-ray spectrum of selenium [Clark and Roach, *Trans. Electrochem. Soc.* **79**, 358 (1941)].

In a, the sharp-lined hexagonal pattern is shown for a sample of very high resistances and no rectifying effect. Patterns b, c and d give typical examples of increasing grain size, accompanied by decreasing resistances and increasing rectification.

be sublimed in a vacuum and obtained in pure form. The element of commerce is usually in lump or rod form. On subliming selenium in air, yellowish vapors have been observed particularly at high temperatures.

Sulfur, selenium, and tellurium are members of the oxygen-sulfur family. They are all bivalent, but also exhibit higher valence states, e.g., tellurium has valences of two, four, and six. Their physical properties are shown in table 29. The specific gravities, melting points, boiling points, allotropicity, etc., all increase with increasing atomic weight.

Chemical Properties

Pure selenium is stable in air, resisting oxidation at ordinary

TABLE 29

COMPARISON OF SULFUR, SELENIUM AND TELLURIUM

	Sulfur	*Selenium*	*Tellurium*
Atomic number	16	34	52
Atomic weight	32.06	78.96	127.61
(Difference)	(47)	(48)	
Atomic volume	16	18	21
(Difference)	(2)	(3)	
Allotropicity	+++	++	+
Density	2.07 (rhombic)	4.5 (cryst.)	6.25
Melting point	114.6°C	217°C	452°C
Boiling point	448.5°C	685°C	1390°C
Metallicity	Non-metallic	Chiefly metallic	Metallic, with limitations
Usual color	Yellow	Brownish	Black
Hydrides	H_2S, most stable, weakest reducing agent of the three.	H_2Se	H_2Te, least stable, strongest reducer
Metallic compounds	CuS, sulfides	CuSe, selenides	CuTe, tellurides
Oxides	S_2O_3, SO_2, SO_4, S_2O_7	SeO_2	TeO, TeO_2, TeO_3
Salts	Sulfites Sulfates Sulfides Sulfides, bi Complexes	Selinites Selenates Selenides Selenides, bi Complexes	Tellurites Tellurates Tellurides Tellurides, bi Complexes

temperatures. It closely resembles sulfur in many of its chemical properties (see table 29). Under the influence of high temperatures and in the presence of hydrogen, selenium forms hydrogen selenide, H_2Se. The action of ozone and water vapor change selenium into selenic acid, the analog of sulfuric acid. When selenium burns in air, the oxide forms. Hydrogen peroxide dissolves finely divided selenium to form selenic acid.

Compounds [1]

Selenium unites directly with the halogens, particularly fluorine, with which it forms a white fluoride. A red-brown liquid, selenium tetrachloride, is produced by the action of

chlorine gas on the element. Selenium also combines with bromine and iodine to form similar compounds. It combines with sulfur to produce a sulfide, and indirectly with nitrogen to form a nitride.

Powdered selenium dissolves readily in cold sodium hydroxide solution, the reactions which take place being very complex, as is the case with sulfur. A purple substance, much like the purple of Cassius, is produced by the deposition of selenium on stannous chloride. Selenium forms coordination compounds and inner complexes which have important analytical applications.

Selenium, like sulfur, enters into many organic compounds, and acts in much the same way as sulfur does.

Biological Nature

Selenium is a highly toxic element, resembling arsenic and antimony in its physiological action. Selenium weakens the heart, causing a decrease in blood pressure, and inhibiting the functions of the central nervous system. Four milligrams per kilo bodyweight, administered to a dog, cause death within a few minutes.

Selenium compounds exert an injurious effect upon germinating seeds. The barrenness of some soils is due to the presence of toxic traces of selenium in the soil. However, the element in small amounts, as with many other poisonous substances, exerts a stimulating effect upon plant growth. The varied applications, as well as the chemistry and physics of selenium, can be found in specialized works devoted to the element.[1]

Technology

About 20 years ago selenium was looked upon as a curiosity, interesting chiefly because it changes its electrical conductivity when exposed to light. Research in recent years led to the development of the selenium "electric eye." The first experiments in the recovery of selenium by American copper refiners

started about 1905, when there was little commercial demand for the metal. Small amounts were used for the manufacture of ruby glass and red enamelware.

In 1910 the annual output of selenium in the United States averaged about 10,000 lb, as against 350,000 lb in 1940. In 1914 experiments were conducted in Europe using selenium for decolorizing glass. It was not until about 1922 that a much larger demand for the element was created through the development of additional applications. The domestic production of selenium has more or less kept pace with copper production, since nearly all of the selenium is produced as a by-product in the copper refineries. Most of the selenium recovered goes into the manufacture of red signal glass. Technically and scientifically important products are the selenium electric eye and the selenium rectifier.[2]

The Selenium Cell

In 1873 Smith, while testing selenium for possible use as a resistor in telephone equipment, found that light striking its surface caused great variations in its electrical resistivity.

Smith was endeavoring to obtain a very high resistance for submarine cables and, knowing that selenium has a high resistance, he experimented with small rods of the substance in lengths of from 5 to 10 cm, and diameters of from 1 to 1.5 mm. These were sealed in an evacuated glass tube with platinum lead-ins.

On testing his selenium resistors Smith found that considerable discrepancy existed between several pieces which should have been identical. On investigating the cause of this discrepancy he found that the resistance varied according to the intensity of light that fell upon the rods. When the rods were fixed in a closed box with a sliding cover, the resistance was highest and remained constant. However, immediately after the cover was removed and light admitted, the conductivity increased from 15 to 100 per cent, according to the intensity

of the radiation falling upon the rods. Smith found that merely intercepting the light with his hand caused an increase in resistance of from 15 to 20 per cent.

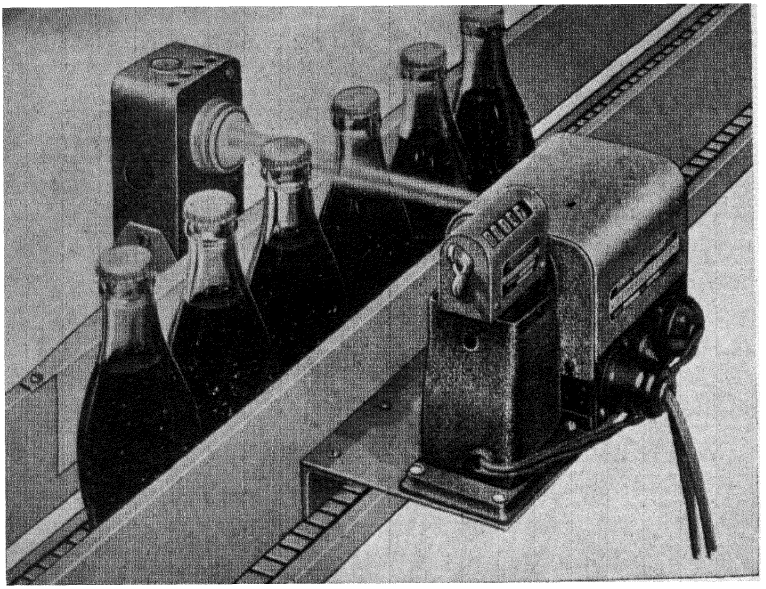

FIGURE 32

Selenium photocells for mechanical counting (courtesy of United Cinephone Corporation).

These experiments gave rise to the original type of selenium cell. It is essentially a circuit containing selenium as an additional resistance element connected to a galvanometer. However, the selenium cell of the present day is a more elaborate piece of equipment. Frequently, photocells have sensitive relays and high-gain amplifying equipment in the circuit.* The

* Selenium cells are not always satisfactory for such circuits, and have been largely replaced by photocells of improved designs, i.e., photo-emissive and gas-filled cells.

selenium in the modern cell is spread in a very thin film over a plate of high purity copper or other metal so that the maximal light effect will be obtained. Filters are often interposed so that the response of the cell may be adapted to specific light sources. Photocells have also been constructed to respond to light in exactly the same way as the human eye does.

The selenium photocell, such as the Weston photronic cell, makes possible the use of light for purposes of measurement and control. It is extremely sensitive to changes in light intensity of all kinds, ranging from the gamma rays of radioactive substances, through X-rays, ultraviolet rays, and the visible spectrum, to infra-red rays and longer wavelengths. An entirely new field in industry has developed with the discovery of the light sensitiveness of selenium.

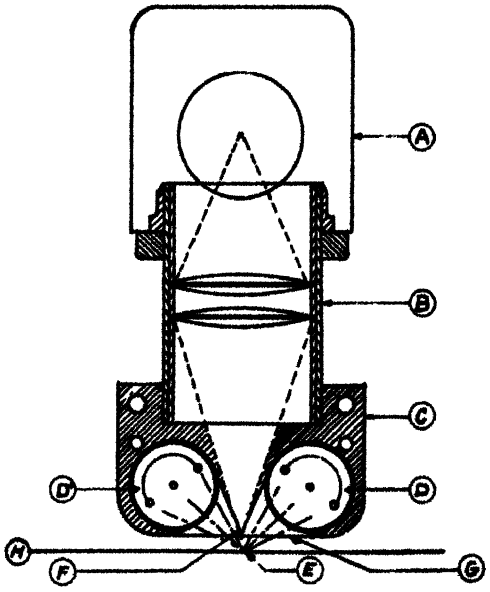

FIGURE 33

Diagram of selenium photoelectric device (courtesy of United Cinephone Corporation).

One of the important uses of the photocell is illustrated by the scanner, a device which consists of a light source and two photocells in a single, compact housing. The scanner eliminates the need for separate photocell and light assemblies, as is often the case in counters and other devices employing the "electric eye."

In the operation of the scanner, light from the bulb in the metal housing (A, Figure 33) passes through the double converging lens in the lens barrel (B), and then through the aperture (F). A concentrated beam of light strikes the surface being scanned (H) and is reflected back into the photocells, its intensity being dependant upon the reflective quality of the scanned surface. Thus, a registration mark on moving paper, or the travel of a meter pointer into the spot of light concentration will cause a change in the illumination reaching the photocells D and D'.

Typical applications of the scanner are registration control from marks imprinted on materials such as plastics, light or heavy opaque papers, cloth, or metals. The scanner is sensitive to cut-off from contrasting colors on similar materials and may be employed for operation through glass from a meter pointer for automatic batch weighing. It may be used in tape reading or repeating on automatic tape machines, detecting the absence or misplacement of labels on tin cans, for paper cutting, box folding, and thousands of other applications.[3]

Selenium cells have permitted rapid advances in many fields. They allow speech over a beam of light. Several forms of apparatus have been invented which allow the blind to read. Selenium cells are also used for high speed counting, delicate laboratory measurements from projected images, remote control, registration control of printing, talking movies, automatic guiding of telescopes, and the trapping of burglars.

The selenium *electric eye* is not so sensitive as the cesium cell, and the current passing through the selenium cell is a

thousand times greater. However, the selenium cell is the most sensitive in the spectral range of the human eye.[4]

Uses in Ceramics

Selenium is important in ceramics, being used both for coloring and for decolorizing glass. For decolorizing glass, selenium is replacing manganese dioxide.

Many tons of selenium are used annually for red glass for automobile tail lights, signal glasses, and other forms of colored glassware. Mixtures of selenium with varying proportions of cadmium sulfide afford a complete series of excellent ceramic pigments ranging from yellow to red.[5]

Colored glasses may be divided into two groups: glasses in which the coloring substance is in true solution; and glasses in which it is in a colloidal state. Colors in the short wavelength visible range, obtained by using manganese, copper, cobalt and uranium, belong to the first group. Those beyond greenish-yellow, i.e., yellow, orange, red, etc., produced by cadmium sulfide and antimony sulfide, and the red produced by gold and selenium, belong to the second group.

It has been found that if the selenium content in glass falls below a certain amount, even a slowly setting, very fluid glass will not show a red color, unles it is kept at a favorable temperature for some time. As little as 0.08 per cent selenium will give a ruby red color. Investigations show that about 75 per cent of the selenium added tends to be lost by volatization. This aspect has been discussed in detail by Krak.[6]

The selenium compounds used in ceramic work are barium selenide, sodium selenite, elemental selenium in the black powdered form, and others. Since the demands for selenium by the glass industry will not increase indefinitely, and as more and more selenium is being recovered from the anode muds in copper refining, the search for new uses of this element continues.

Rubber Applications

Selenium finds application in the rubber industry for vulcanizing, being employed as a secondary agent mixed with sulfur for tire-carcass stocks, friction belts, oil resisting stocks, wire insulators, clothing, electricians' gloves, and motor mounts.

Small amounts of selenium impart to rubber several desirable properties which cannot be obtained with sulfur. Selenium is employed along with tellurium to toughen rubber. The toughening properties are ascribed more to the tellurium, but a superior type of vulcanization results when it is combined with selenium and used as a substitute wholly or partly for sulfur.

Uses in Alloys

Both selenium and tellurium are employed to improve the machinability of copper and copper alloys and to a very small extent as modifying agents in corrosion-resistant steels.[7]

Tyler has pointed out that additions of selenium have been made successfully to 18/8 steels whose work-hardening properties tend to develop extreme surface hardness as soon as they are worked. The improvement is similar to that obtained by additions of sulfur, but is without the deleterious effect of sulfur on corrosion resistance and mechanical strength. The steel industry is a most promising outlet for selenium, and the production of the element will depend considerably on the demands of this industry. Much more selenium might be employed than is now used, especially in free-cutting steels, replacing Bessemer screw stock. In copper alloys selenium improves machinability without hot-shortness and in copper it does not cause cold-shortness. Selenium has comparatively little effect upon the tensile strength and reduces the ductility only slightly.[8]

Other Uses

Selenium has been used on a small scale for fireproofing fabrics, wood, and other inflammable materials. However, such applications have not met widespread use and it is likely

that in the face of stiff competition by other less expensive substances, development in this field is not imminent.

Rectifiers containing selenium elements are available on the market. These are claimed to be superior to other devices of a similar kind. They are being employed in telephone communication, as well as for large-scale industrial rectification. Suggested applications for selenium rectifiers and like equipment are specialized and include magnetic clutches, solenoid valves, alarm signal and communication systems, and isolated direct current motors.

Diethyl selenide has been proposed as an anti-knock agent for gasolines. At present the compound has not gained favor over lead tetraethyl. Colloidal selenium finds limited application as a fungicide and germicide for plants and animals. Selenium compounds have been employed for the preservation of wood. In connection with this use, it is highly probable that selenium compounds could serve in place of sulfur for insecticidal purposes.

Analysis

There are a number of methods for detecting and determining selenium and, as would be expected, the procedure varies according to the amount of element present and type of material. In the gravimetric determination of selenium, the results are generally obtained by weighing the selenium in the elemental form.[9] Selenium is thrown down from its solutions by treatment with sulfurous acid in hydrochloric acid,[10] or with potassium iodide in acid solution.[11] Several other reducing agents may be employed. Selenium can be determined volumetrically, although some techniques are rather involved and, as results are obtained indirectly, many analysts prefer to employ gravimetric or other procedures.

In testing for selenium, 1 cc of 5 per cent ferric chloride solution is added to 2 cc of the solution to be tested and the whole diluted to 10 cc with syrupy phosphoric acid. To this

solution 5 to 10 drops of a 1 per cent ethanolic pyrrole solution are added. In the presence of selenium ions a deep blue coloration develops.[12]

In testing for selenium a small particle of the solid seleniferous material is placed in a porcelain dish and 1 drop of 5 per cent thiourea solution is added. After mixing, 1 drop of 1N hydrochloric acid is added. A red precipitate forms if the selenium ion is present.

For detecting selenium in natural waters, the procedure is to evaporate a 60 cc sample to about 4 cc and add 5 drops of concentrated hydrochloric acid. The residue is transferred to a small graduated cylinder and its volume made up to 6 cc with the wash water. It is filtered, and to 5 cc of the clear filtrate 2 drops of concentrated hydrochloric acid and 5 drops of 5 per cent thiourea solution are added. It is boiled and allowed to cool for 5 minutes. The formation of a red precipitate is indicative of selenium. If the water contains sodium bicarbonate a small amount of dilute hydrochloric acid is added to acidify it.[13]

In testing urine for the presence of selenium,[14] 100 to 500 cc of urine are treated with 25 cc of concentrated nitric acid and 30 cc of 30 per cent hydrogen peroxide. The mixture is slowly warmed until foaming ceases and evaporated to dryness on a water bath. If the residue is darker than a light yellow color it is treated with 10 cc of hydrogen peroxide and evaporated again.

The residue is treated with 10 cc of 25 per cent hydrobromic acid colored a straw yellow with about ½ drop bromine. Without warming, the solution is filtered through asbestos and 0.25 to 0.5 g sodium bisulfite, hydroxylamine hydrochloride, or hydrazine sulfate is added to the filtrate, with gentle warming for 15 minutes, and allowed to stand for from 1 to 3 days. A pink precipitate indicates the presence of selenium.

A reagent for selenium is a solution of 10 g mercuric nitrate in 10 cc of nitric acid and 100 cc of water. Crystalline precipi-

tates are formed with selenic acid and soluble selenates.[15]

To test for selenium in the presence of large amounts of sulfur, the sample is heated with an excess of manganese dioxide and the evolved gas conducted into water. The water is then agitated with manganese dioxide. After the odor of sulfur dioxide disappears, an odor like that of decayed horseradish indicates the presence of selenium.[16]

The thiourea test of Falciola [17] for selenium is sensitive to 1 part in 1,000,000. A little thiourea is placed on filter paper and allowed to run into the seleniferous solution. The development of an orange-red precipitate indicates selenium, although in great dilution only a red color forms.

Codeine furnishes a good organic reagent for selenium. A fraction of a milligram of selenium in sulfuric acid turns green in the presence of codeine.[18]

Another test for selenium in urine is made by adding 1 or 2 cc of stannous chloride solution to 10 to 15 cc of urine and extracting by shaking with an equal volume of ether. The ether is drawn off and evaporated. Any selenium present adheres to the glass wall in the form of a red deposit.[19]

A convenient test for selenium is that of Feigl and his coworkers:[20] on a spot plate mix 4 drops of a 1 per cent glacial acetic acid solution of diphenylhydrazine, 1 drop of 2N hydrochloric acid, and 1 drop of the solution to be tested. A red coloration develops in the presence of selenium.

In testing minerals the procedure is to take a small amount of the finely powdered sample and place it in a small crucible, adding 3 to 4 drops of 30 per cent hydrogen peroxide, then an equal amount of hydrochloric acid, and heating until the sample is practically dissolved. Evaporating to dryness is the second step, then adding 3 to 4 drops of hydrochloric acid and a little oxalic acid, and finally evaporating down as before. Feigl's reagent is applied to the residue.

A procedure for detecting selenium in organic compounds is to digest 1 g of the dried sample with 40 cc of sulfuric acid

and 0.2 g of mercuric oxide until colorless. After cooling and adding sulfuric acid to make the volume 50 cc, 2 drops of 3 per cent aqueous codeine sulfate are added to 5 cc of the solution. The solution is cooled and shaken after the addition of each drop of codeine solution. A green coloration changing to blue indicates the presence of selenium.[21]

One part of selenium in 20,000,000 can be detected by adding 5 cc of concentrated hydrochloric acid and 2 cc of 0.25N ammonium thiocyanate, and diluting to a volume of 10 cc with water. The solution is heated to boiling and boiled for 1 minute longer. If selenium is present, a red, green or yellow precipitate forms, depending on the concentration of the element.[22]

On adding 0.1 g of sodium hydrosulfite to 1 cc of a weakly acid *selenic* solution, a yellow-red coloration forms. Adding sodium carbonate removes any orange coloration due to hydrosulfurous acid. The test is sensitive to 1 part in 20,000. On adding sodium hydrosulfite to sulfuric acid, the sulfur is precipitated and colored red by any selenium that may be present if *selenous* acid is present in the sulfuric acid.[23]

Selenium, often an impurity in sulfuric acid, may be detected by adding a small crystal of aspidospermine to 1 drop of the acid. In the presence of selenium a deep violet color diffuses through the liquid.[24]

Tellurium

History

In 1782, Mueller von Reichenstein, an Austrian chemist, found a peculiar metal in gold ore obtained from what is now known as Transylvania in Austria. Doubtful of his discovery, von Reichenstein sent samples of the ore to the Swedish chemist Bergmann, who confirmed the presence of an unknown metal in it. Bergmann showed that it was not stibnite (anti-

mony sulfide), although he did not exclude the possibility that it was an antimony compound.

Not satisfied with the result of Bergmann and seeking more positive confirmation, von Reichenstein sent specimens of the same ore, about 16 years later, to the expert analyst Klaproth. Klaproth immediately confirmed the existence of the new element and named it tellurium from the Latin word *tellus*, meaning the earth.

In 1832, 34 years after the investigations of Klaproth, Berzelius prepared many compounds of the element. It was partly due to his familiarity with the work of Klaproth that Berzelius was able to distinguish selenium from tellurium in ores in which they are both found in close association.

The investigations of Berzelius on both tellurium and selenium are significant because rapid advances in the classification of the elements were made possible. By preparing the more important compounds of these elements, it became possible to show that selenium and tellurium resemble sulfur. All of these elements, together with oxygen, now comprise a common family in the periodic table. Many years later the discovery of polonium extended this series.

Mineralogy

Like selenium and sulfur, tellurium often occurs in the native state. It is widely distributed but not in large amounts in any one locality. Tellurium is found in the flue dust from smelters working gold telluride ores, and in the flue dust from zinc processing. The usual natural combinations of tellurium are with gold, silver, lead, mercury, and bismuth. When the element is native it is frequently crystalline, being up to 98 per cent tellurium with an admixture of impurities such as gold, silver, copper and other metals.

Native tellurium is found in many of the mines in Boulder County, Colorado. The most prominent telluride is probably

sylvanite, although there are several others such as hessite, petzite, calaverite, and tetradymite. These minerals were first discovered in large amounts in Hungary and Transylvania and later in the United States. The state of Colorado is extremely rich in gold and silver tellurides. Other states such as South Dakota, Oregon, Montana and California also produce telluride ores.

The occurrence of sylvanite $(Au, Ag)Te_2$ was first noted in the Red Cloud mine at Gold Hill, Boulder County, Colorado, and later in other mines in the state.[25] Sylvanite is a telluride of gold and silver, and is often associated with lead and antimony and other base metal ores. Some of the early mines of Colorado were fabulously rich in various gold and silver tellurides.

TABLE 30

TELLURIUM MINERALS

Mineral	*Composition*	*Per Cent Te*
Calaverite	$(Au,Ag)Te_2.AuTe$	56–58
Coloradoite	$HgTe$	36–39
Durdenite	$Fe_2(TeO_3)_3.4H_2O$	47–64
Grunlingite	Bi_4TeS_3	12–13
Krennerite	$(Au,Ag)Te_2$	38–59
Melonite	$NiTe_2$	73–76
Rickardite	Cu_4Te_3	59–60
Tellurite	TeO_2	79–80
Tellurium	Te	93–97
Tetradymite	$Bi_2Te_2S_3$	33–49

An important tellurium mineral known as calaverite was first found in the Stanilaus mine in Calaveras County, California. It is found as a brittle, yellowish-gray solid, often having a bronzy tinge and a massive form. Calaverite has an uneven subconchoidal fracture and it burns on charcoal with a bluish-green flame, yielding globules of bright yellow gold.

The minerals petzite, $(Ag,Au)_2Te$, and hessite, Ag_2Te, are

natural alloys of the two (or three) metals. They are much like sylvanite, having a massive form, conchoidal fracture, and a metallic luster, with a hardness of about 2.51 and a specific gravity ranging from 9 to 9.4.

Hessite, however, is silver telluride and contains little or no gold. It is invariably associated with native gold, quartz, and a rare telluride of lead known as altaite, PbTe. Hessite has a lead-like color and is massive. Its hardness varies between 2 and 3.5 and its specific gravity between 8.3 and 8.6. Its fracture is even and it has a metallic luster.

Tetradymite (bismuth telluride) is found in several localities throughout the country. Tellurium is found in many minerals as an impurity and is associated in nature with selenium, sulfur, some of the iron minerals, such as pyrite, and in arsenic and zinc ores. It is recovered from the mud of sulfuric acid chambers and from the anode mud of copper refineries.

Most of the telluride minerals have relatively low melting points, and it is generally possible to remove the tellurium by reducing the mineral on a charcoal block with the mouth blowpipe. With the aid of the blowpipe and charcoal block it is possible to distinguish many of the tellurium minerals. For example, hessite and sylvanite can be readily distinguished by this method. The powdered mineral is placed on a smooth charcoal block and heated to redness to drive off the tellurium. The residual globules of metal may be distinguished by the aid of a low-power magnifying lens.

In the early days of prospecting for telluride ores in Colorado, it was customary for the miner to place a large lump of suspected gold or silver telluride in a blacksmith forge and heat strongly. If gold and silver were present they would come to the surface of the mass in globules. Some of the early-day gold telluride ores of Colorado contained over $100,000 in gold per ton.

No attempt has been made to list, in table 30, all the known tellurium minerals; some are doubtful species, while others

appear to be mixtures. Table 31 gives a typical analysis of some of the better known tellurides of lead, gold and silver.

Tellurides as well as selenides occur in copper-bearing ores (chalcocite and chalcopyrite). At present these copper ores are the chief source of tellurium and selenium.

TABLE 31

GOLD, SILVER AND LEAD TELLURIDES

Element	*Sylvanite*	*Petzite*	*Altaite*	*Hessite*
Tellurium	44.5- 59 9	31.5–34.2	37.3	38.1
Antimony	8.5 0.6	—	—	—
Lead	11.2- 0.2	- -	60.7	0.2
Gold	26.9–25.3	24.8–42.4	0.3	0.2
Silver	11.5–10.5	40.6–42.4	1.2	60.2
Copper	0 – 0.8	- -	—	0.2
Iron	0 – 4.5	—	—	1.2
Zinc	—	- -	—	trace

Physical Properties

Tellurium is a brittle, silvery-gray, metallic solid that exists in several allotropic forms. The most familiar allotropes are the stable medium-gray crystalline solid with a metallic luster and an amorphous form. Tellurium resembles a semi-metallic element in many of its physical and chemical properties, although at times it acts like a true metal. Its appearance is somewhat like antimony and when pure and granular may be difficult to distinguish from it.

The atomic weight of tellurium is 127.61, although a great deal of controversy precluded this determination made by Hönigschmid. At the time Mendeleeff enunciated his periodic law, and until Moseley's classic work on atomic numbers, iodine and tellurium were not established in the periodic table with certainty because of conflicting atomic weights. Tellurium, being heavier than iodine, was placed with the halogens and iodine was placed with selenium and sulfur. Although Men-

deleeff righted this arrangement, he believed that one or both atomic weight determinations were incorrect.

Physically speaking, tellurium is a very complex element, being made up of eight isotopes of masses 120, 122, 123, 124, 125, 126, 128, and 130. The abundance of tellurium isotopes is as follows:

TABLE 32

ABUNDANCE OF TELLURIUM ISOTOPES

Te	*Per Cent*
120	0.1
122	2.9
123	1.6
124	4.5
125	6.0
126	19.0
128	32.8
130	33.1

Tellurium melts at 452°C. The specific gravity of the crystalline form is 6.25. It boils in hydrogen at 1390°C. Tellurium, like the remaining members of the sulfur family, sublimes rather easily at higher temperatures.

Chemical Properties

It may be noted from table 29, comparing the chemical properties of selenium and sulfur, that tellurium forms compounds and reacts very much like selenium and sulfur. Tellurium is readily distinguished from selenium by its behavior under the blowpipe. This simple test can be employed to differentiate the two in the field. Tellurium, when heated, forms an oxide which has a strong acidic odor, whereas the dioxide of selenium formed from heating has an odor like that of decayed horseradish.

Elemental tellurium is stable in air at ordinary temperatures.

It forms the dioxide when heated in air or allowed to burn in oxygen. It burns with a green flame. Tellurium is not affected by hydrochloric acid, but sulfuric acid attacks it, with the evolution of sulfur dioxide. It is oxidized by nitric acid and aqua regia to tellurous acid, H_2TeO_3, the analog of sulfurous acid. When tellurous acid is dissolved in sodium hydroxide, it forms the compounds Na_2Te and Na_2TeO_3. Tellurium combines with metals to form tellurides. Several alloys of tellurium have been prepared.

Compounds

Selenium and especially tellurium are on the borderline between metals and non-metals. They form compounds of the same type, including hydrogen compounds analogous to water. The hydrides are ill-smelling gases at ordinary temperatures. Their acidity increases with increasing atomic weight. Table 33 shows the similarity of the hydrogen derivatives of oxygen, sulfur, selenium, and tellurium.

TABLE 33

PROPERTIES OF WATER ANALOGS

	Molecular Weight	*Melting Point, °C*	*Boiling Point, °C*	*Specific Gravity*	*Dissociation Temperature, °C*
H_2O	18.02	0	100	1	1800
H_2S	34.09	–85.5	–61.8	1.17	400
H_2Se	81.22	–64	–42	2.81	150
H_2Te	129.52	–48	0	2.57	0

Technology

Tellurium metal is readily prepared. At some of the copper refineries, selenium and tellurium are converted into the selenite, selenate, tellurite and tellurate of sodium. The alkaline solution of the two metals is neutralized with sulfuric acid. A precipitate of TeO_2 is formed, which is collected on a film. Selenium in the filtrate is precipitated as red elemental sele-

nium by passing SO_2 into the filtrate. The TeO_2 precipitate is dissolved in strong hydrochloric acid, then diluted with water, and SO_2 is passed into the solution. Tellurium metal is precitated as a gray powder.

One of the copper companies dissolves the TeO_2 in caustic soda solution and plates out metallic tellurium as a steel-gray, brittle cathode deposit. This alkaline electroplating bath is preferable to the fluoride bath.[26]

Tellurium-Lead

The development of tellurium technology has been very slow. Like selenium the output of the element depends upon the demands of the steel industry. Tyler [7] has reported wider use of tellurium-lead, an alloy consisting mostly of lead but having a small admixture of tellurium, usually 0.02 to 0.085 per cent. Tellurium imparts hardness, toughness, and increased corrosion-resistance to lead. Only 50 to 75 tons of tellurium annually would be sufficient to treat all the lead used in the United States for chemical plants and for general building construction.[27]

Alloys

Tellurium also imparts desirable properties to other metals. Plain carbon steels and other alloys become more machinable when small amounts of tellurium are present. A small amount is employed to increase the free-cutting properties of steel alloys. Tellurium lead is valuable for lining tanks and for acid pipes and coils in plants handling sulfuric acid and hot chromic acid solutions. Tellurium lead costs only a fraction of a cent per pound more than ordinary lead.

When tellurium is alloyed with tin a metal is obtained which has increased tensile strength and hardness. The tellurium alloy of aluminum is very ductile. Silver alloyed with tellurium is at present just a laboratory curiosity, but it possesses valuable properties.[28]

In addition to the remarkable hardening properties imparted

by tellurium to tin, the creep-strength also increases. A development with possibilities is the improvement of the quality and life of chilled-iron car wheels. Tellurium and graphite are added in small amounts to each ladle of molten iron as the metal is cast.[29]

Small amounts of tellurium, in a concentration of about 0.5 per cent, are available on the market in the form of a copper alloy. This alloy is claimed to have superior qualities of free-machinability and forgeability.[30]

Other Uses

Tellurium increases the toughness and resistance of rubber to abrasion. Hose coverings and electrical insulators containing tellurium are now made on a small scale. Tellurium is not as strong an accelerator as selenium, so it must be added in larger quantities. Tyler has pointed out that tellurium is to be recommended where low-sulfur compounds are required and where heat-resistance is an important factor.

Tellurium is used in electrolytic zinc plants to remove cobalt by the Tainton process, but as crude tellurium-bearing slimes seem to be equally effective, the use of pure metal for this purpose has declined.

Marden, Beese, and Meister[31] have developed a tellurium-vapor lamp similar in principle to the mercury-vapor lamp. Although the lamp is still in the early stages of development, it may be important as a continuous source of light resembling day light.

Like those of selenium, a few tellurium compounds have antiknock properties, although there is no extensive use of these substances at present. Colloidal tellurium possesses fungicidal qualities. Tellurium has been used in dental fillings when alloyed with silver and gold. It is used, like selenium, to a limited extent in coloring glass. The dioxide imparts a white opaqueness to some glasses. Tellurium compounds have been used as dyestuffs. The element has also been employed for toning prints in photographic work, particularly silver prints.[32]

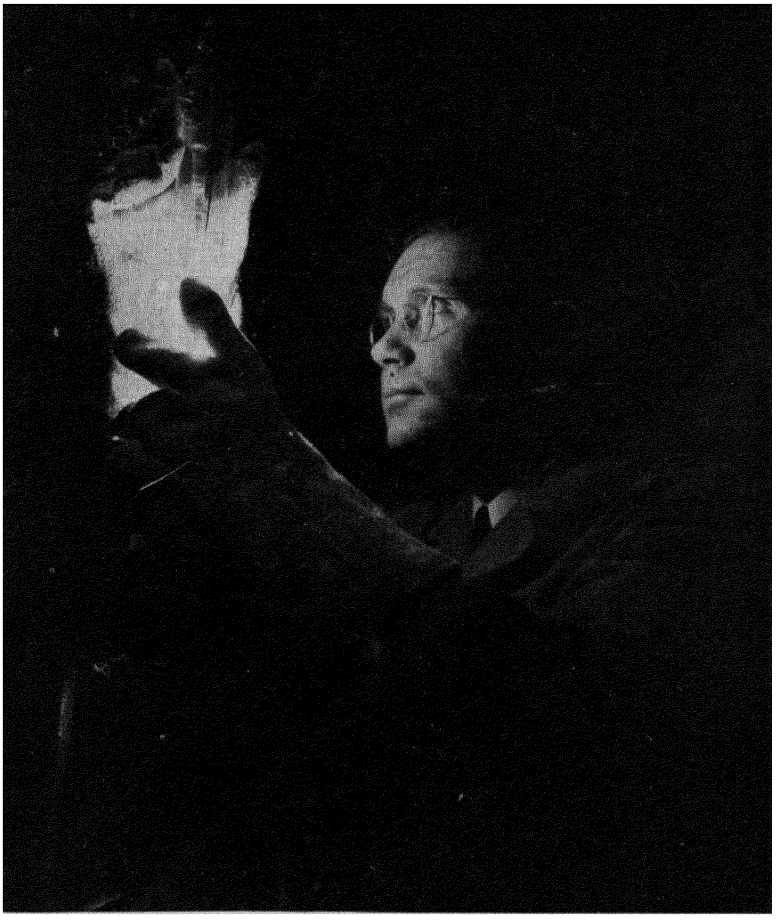

FIGURE 34

Tellurium vapor discharge lamp (courtesy of Westinghouse Electric Company).

Analysis

Tellurium is determined gravimetrically much like selenium in that it is isolated and weighed in elemental form. Tellurium is obtained by treating solutions containing the element with

the following reagents: sulfur dioxide, hydrazine sulfate in ammonical solution, potassium iodide and sulfur dioxide, sugar in alkaline solutions, and others.[33]

Tellurium may be weighed as the sulfate, which is obtained by treating elemental tellurium with a mixture of nitric and sulfuric acids, evaporating to incipient dryness, and desiccating.

Tellurium may be determined volumetrically by the reduction of telluric acid to tellurous acid by potassium bromide in sulfuric acid solution; bromine is passed into potassium iodide and the iodine determined by the standard thiosulfate method.

In detecting tellurium in tellurides, for example, a small particle of the substance to be tested is placed in a porcelain dish and one drop of concentrated sulfuric acid is added. On gentle heating a beautiful carmine red color develops when tellurium is present. This coloration is due to the formation of tellurous oxide, which dissolves in the sulfuric acid. The odor of sulfur dioxide will also be noted. When water is added to the solution, metallic tellurium is precipitated as a grayish powder.

An excess of ammonium chloride and magnesium chloride form a crystalline precipitate with solutions containing selenite and an amorphous precipitate with solutions containing tellurite.[34] Metallic tellurium is precipitated as a blackish powder on heating tellurous acid in an alkaline solution, using glucose as the reducing agent.[35] This reaction is also given by selenous acid.

Another test for tellurium is to place a little thiourea on filter paper and allowing a drop of the test solution to fall on it. In the presence of tellurium a yellow spot forms. Moderately concentrated solutions of tellurium form a crystalline yellowish precipitate with thiourea. Very dilute solutions are colored yellow. This test is claimed to be sensitive to 1 part tellurium in 500,000.[36]

A reagent for detecting tellurium consists of a solution of 25 g of cadmium acetate in 200 cc of acetic acid, diluted to 1 l

with water. The procedure is to pour a solution of 10 g of potassium thiocyanate in 100 cc of water on the material to be tested, warm, add ethanol and then the reagent.[37] Members of the sulfur family give varying reactions. Sulfur forms a yellow precipitate, selenium an orange-red precipitate, and tellurium a gray-black precipitate.

Another test for tellurium in minerals depends upon the formation of red tellurous sulfite.[38] When copper is added to a dilute solution of the powdered mineral in concentrated sulfuric acid, the red color forms.

Tellurium and selenium may be tested singly in the presence of one another. To detect selenium in the presence of tellurium, filter paper is moistened with a drop of concentrated hydriodic acid and then a drop of the solution to be tested is placed in the middle of the moist spot. If selenium is present, a black coloration develops. The spot is then decolorized with a drop of sodium thiosulfate solution and the red spot of selenium is noted. Under these conditions no tellurium reacts. The tellurium is deposited by the action of stannous chloride in the prescence of sodium hydroxide and selenium is not.[39]

Tellurium in the presence of acetate or acetic acid, when in the form of the tellurite ion, is decomposed by titanium trichloride with the evolution of ill-smelling hydrogen telluride.[40]

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CHAPTER VII

PLATINUM, PALLADIUM, RHODIUM, IRIDIUM, OSMIUM, RUTHENIUM

Early History of the Platinum Metals

The platinum metals usually occur together and appear to have been known as *a metal* to the Greeks, although there is no conclusive evidence that they attached any importance to the metal.[1] A metal called aluta, possibly platinum, is mentioned by Pliny.

The first authentic reference to platinum seems to be that of Julius Caesar Scaliger in his book *Exotericarum Exercitationum de Subtilitate*, published in 1557, in which mention is made of a white infusible metal found in the silver mines of Mexico. The term *platina del pinto*, meaning silver-like metal from the Pinto River, has been in general use for a long time by the Spaniards of South America.

The first specific reference to platinum, however, was made by Don Antonio de Ulloa, a Spanish naval officer, in his narrative about a journey to South America in 1735. Ulloa obtained specimens of platinum from the gold-bearing sands of the Pinto River, near Papayand, Columbia. Platinum had been in use long before the arrival of Ulloa by the natives of the Papayan district, who collected grains of native platinum, along with gold from alluvial deposits, and fashioned them into crude tools and instruments. In some parts of Columbia, ornaments made of platinum have been found in ancient ruins.

During the time of the Spanish conquests in South America, platinum was much less valuable than gold, hence it was often

used for counterfeiting gold, due to its high specific gravity. Early Spanish gold seekers and traders often gold-plated coins made of platinum. As a result of this fraud, the Spanish government forbid the export of platinum from South America, and ordered all stocks of the metal thrown into the ocean.

The first platinum was brought to Europe in 1741 by Wood. His platinum nuggets finally fell into the hands of a chemist, Watson, in 1750. Watson studied the metal and recognized it as a new substance, but he failed to learn its true nature. Smith [2] has pointed out that when the crude metal was first introduced into Europe it was marketed under the name of "white gold."

Watson [3] published his account of platinum in 1750, two years after Ulloa's narrative had appeared. In 1752 Director Scheffer, of the Stockholm Mint, acquired some of the metal for study. His studies marked the first real elucidation of the character of the white metal. He showed that platinum is insoluble in acids, but is readily attacked by aqua regia.

Later researches, in 1757, by Marggarf showed that platinum is precipitated from its chloride by the addition of potassium or ammonium salts, but not by sodium salts. Old as this work is, it forms the basis of most present day knowledge of the metal. Macquer and Beaumes [4] showed in 1758, that the metal could be fused. Later, other experimenters found that platinum could be made into crucibles and used very successfully in chemical work. From 1800 on, it was demonstrated that the metal could be drawn into fine wire, rolled, and annealed, thus leading to its commercial applications. It has a high fusibility and resists most chemical agents.

However, owing to the difficulty of fusing platinum, little use could be made for the metal in the industries and arts until 1847, when Hare of Pennsylvania, inventor of the oxyhydrogen blowpipe, showed that platinum could be fused and worked with the great heat of his blowpipe. Hare fused as much as 2 lb of platinum sponge (on charcoal) at one time, a considerable advance over the former swaging method with a white-

hot sponge, which was depended upon to obtain compact metal for rolling and wire production. As a result of the work of Hare, the platinum industry assumed considerable importance, and by 1876 platinum took its place with the other precious metals.

Palladium and Rhodium

In 1803 the great English chemist, Wollaston, demonstrated that the platinum used in all previous studies was a mixture or an alloy. He succeeded in separating the metals palladium and rhodium from the mixture. This investigator made systematic studies of the platinum metals. These studies resulted in the discovery of the remainder of the platinum metals by other chemists. Wollaston chose the name *palladium* in honor of the newly discovered planet Pallas, and the name *rhodium* in allusion to the rose-red color of solutions of some of this metal's salts.

Osmium and Iridium

While Wollaston was working upon platinum, palladium, and rhodium, Tennant found that two other metals were also present. In 1804 Tennant isolated osmium, the metal deriving its name from the Greek word for smell, because of the obnoxious odor of the tetroxide. Tennant also found iridium during the year 1804.

Ruthenium

Finally, in 1845, the Russian chemist Klaus detected a fifth metal in the osmiridium portion of crude platinum group. He named it ruthenium in honor of Ruthenia, in Russia.[5]

Mineralogy of the Platinum Metals

Platinum, osmium, iridium, palladium, rhodium, and ruthenium, members of the platinum group of metals, usually occur native and in the form of natural alloys. Platinum occurs in

alluvial deposits together with gold. It is associated with various ore deposits where it may be recovered as a by-product. The platinum metals are frequently associated with chromite and olivine in peridotite rocks, but in quantities too small to enable profitable working for their metal content.

The platinum metals form a well-defined natural group of elements, which are found associated with one another, and with copper and nickel minerals. With few exceptions the platinum metals occur native, or in alloys, which vary in composition and have received numerous specific names. Platinum-group minerals include sperrylite ($PtAs_2$) and laurite (RuS_2).

The literature on the platinum group of metals includes references to numerous sub-species, owing to varying amounts of the metals present. The native metals and alloys may be grouped as follows:

Platinum
Iridium and platiniridium
Palladium and allopalladium
Iridomine { nevyanskite, containing over 40 per cent iridium; siserskite, containing less than 40 per cent iridium }
Palladium-gold
Rhodium-gold

Native platinum is never pure; it is always alloyed with other members of the platinum group, and various other metals. Numerous analyses of native platinum from localities throughout the world show a varying platinum content, ranging from about 56 per cent to 86.33 per cent. Buddhue [6] has pointed out that the purest platinum is found in the placers of the Iset River, Siberia, and contains 86.33 per cent platinum. Iridium, palladium, and ruthenium are present in practically all samples of native platinum. So characteristic are the impurities in native platinum, that the locality can frequently be determined from the analysis alone.

Iridosmine (osmiridium) is an alloy of iridium and osmium of varying composition. The iridium content may be 77 per cent or greater, or as low as 40 per cent. One analysis of iridosmine from the Ural Mountains gave 43 per cent iridium and 48 per cent osmium; while another analysis of Ural iridosmine, gave 77 per cent iridium and 21 per cent osmium. Usually, the platinum content is less than 1 per cent. Rhodium and ruthenium are usually present in small amounts.

The osmite of Borneo is nearly pure osmium, usually about 80 per cent, containing about 10 per cent iridium and 5 per cent rhodium. The term osmite is sometimes applied to iridosmine containing over 40 per cent osmium.

TABLE 34

COMPOSITION OF NATIVE PLATINUM *

	Russia, Urals	*Colombia, S. A.*	*British Columbia*
Platinum	76.22–86.05	76.82–86.20	72.07
Iron	6.54–17.30	7.20– 7.80	8.59
Palladium	0.75– 1.94	0.50– 1.14	0.19
Rhodium	0.96– 3.17	1.22– 2.50	2.57
Iridium	0– 0.98	0.85– 1.55	1.14
Copper	0– 0.86	0.60– 0.88	3.39
Osmiridium and volatile matter	0.50– 2.10	0.95– 7.98	10.51
Osmium	0– 0.54	—	—
Gold	—	1.00– 1.50	—
Sand	—	0.95– 4.35	1.69

* After E. A. Smith, *The Platinum Metals*, London, 1924.

Native palladium occurs in grains having a radiated fibrous structure. It is found in platinum concentrates from various localities, including Brazil and the Ural Mountains. It is always alloyed with a small amount of platinum and iridium.

Allopalladium is said to be a rhombohedral allotrope of palladium, but there is evidence to indicate that it may be an alloy of palladium and mercury, and/or selenium.

Rhodium is generally recovered from other members of the platinum group, but the rare rhodium-gold alloy (rhodite) is said to contain from 34 to 43 per cent rhodium.

A few naturally occurring compounds of the platinum group are known. The most important is sperrylite, an arsenide of platinum containing small amounts of rhodium and traces of palladium. Sperrylite was first discovered in the Sudbury, Ontario district, and described in 1889 by Wells. Since then it has been reported in Georgia, Wyoming, Siberia, South Africa, and elsewhere. The sperrylite of South Africa occurs as minute crystals having a bright, tin-white luster.

Cooperite, a sulfo-arsenide of platinum, occurs in the Merensky Reef of South Africa, associated with sulfides of the base metals. An analysis of cooperite by Buddhue[7] gave 64.2 per cent platinum, 9.4 per cent palladium, 17.7 per cent sulfur, and 7.7 per cent arsenic.

Stibiopalladinite occurs in association with cooperite in the Merensky Reef. An analysis by Adams gave 70.4 per cent palladium and 26.0 per cent antimony.

Laurite, a sulfide of ruthenium and osmium, was first discovered in the gold and platinum placers of Borneo, and was later reported in the gold placers of Port Orford and Curry County, Oregon, and Colombia, South America. It usually occurs as small black octahedrons, difficult to distinguish from magnetite, owing to the minute size of the laurite crystals. Even in the concentrates from the placers, laurite occurs only very sparingly, making the isolation of pure material for analysis difficult.

Although platinum-bearing sands and gravels occur widely in Alaska, British Columbia, Oregon, and California, the deposits are generally not rich enough to be worked for the platinum content alone. Usually the platinum group of metals are recovered as a by-product in the gold placers. The huge gold dredges operating in the west also recover an appreciable amount of the platinum group of metals. Much larger quanti-

ties of platinum metals are obtained in the United States as by-products in the refining of other metals.

Much of the platinum consumed in the United States originates in foreign deposits. It is often imported in crude form for domestic refining. For many years the Ural Mountain mines of Russia have contributed heavily to the world production of platinum. Colombia, South America, has also been a heavy producer. Since the development of the mines of the Sudbury districts in Ontario, Canada, most of the platinum of commerce is today recovered from these nickel-copper ores as a by-product. For a number of years the Sudbury production of the platinum group of metals has dominated the world market. The mines of the Union of South Africa have also made small, though notable contributions to the world's supply of platinum-group metals.

Platinum Metal Groups

The six members of the platinum metal family fall naturally into two groups. The three lighter metals, ruthenium, rhodium, and palladium, resemble silver. The atomic number of these elements increases from 44 for ruthenium up to 47 for silver. Their atomic weights and physical properties also increase with the atomic number. The outstanding similarity of these metals is their specific gravity of about 12.0, although the value may vary slightly with the form of the metal (see table 35).

In the second group, the three heavier metals and gold are very much alike in their physical properties. The atomic number of these metals increases from 76 for osmium up to 79 for gold. The specific gravity of the heavy-group metals is about 22. The densest substances known are included in this group. In the light-group metals the valences do not vary regularly, but in the heavy group, the number of valences for each element decreases with an increase in atomic weight (see table 36).

TABLE 35

PHYSICAL PROPERTIES OF THE LIGHT GROUP OF PLATINUM METALS

Property	*Ru*	*Rh*	*Pd*	*Ag*
Atomic number	44	45	46	47
Atomic weight	101.7	102.91	106.7	107.880
Isotopes	7	2	6	2
Atomic volume	8.3	8.5	8.9	10.1
Valences	2, 3, 4 6, 7, 8	2, 3, 4	2, 4	1, 2, 3
Specific gravity	12.26	12.5	12.0	10.5
Melting point	2450°C(?)	1966°C	1555°C	960.5°C
Boiling point	2870°C(?)	2500°C(?)	2540°C(?)	1950°C
Brinell hardness	220	139	49	25

TABLE 36

PHYSICAL PROPERTIES OF THE HEAVY GROUP OF PLATINUM METALS

Property	*Os*	*Ir*	*Pt*	*Au*
Atomic number	76	77	78	79
Atomic weight	190.2	193.1	195.23	197.2
Isotopes	7	2	5	1
Atomic volume	8.5	9.1	9.1	10.1
Valences	2, 3, 4, 8	2, 3, 4	2, 4	1, 3
Specific gravity	22.48	22.4	21.45	19.31
Melting point	2700°C	2454°C	1773.5°C	1063°C
Boiling point	5300°C	4800°C	4300°C	2600°C
Brinell hardness	—	172	47	45

Extraction of Platinum Metals

Two facts are encountered in the extraction of platinum metals from their ores which are not common to the other elements. In the first place, the platinum metals are not available in large amounts even in concentrates, and the concentrates are of comparatively low value. In the second place, the platinum crudes do not respond to ordinary chemical reagents, amalgamation, cyaniding, and other modes of treatment being valueless.

For extracting platinum a long and tedious operation must be performed under expert supervision. Generally, platinum extraction requires the use of aqua regia or special methods of smelting and fluxing with lead oxide. The latter technique is rarely used.

Opening Platiniferous Ores

One method of opening platinum ores is to treat a heated mixture of the platiniferous material and sodium chloride with chlorine gas. All of the platinum metals are attacked, giving rise to double chlorides of the metals with sodium. These double chlorides differ in stability, variations in treatment and temperature producing different products. When a double chloride is decomposed at or below the temperature of formation, the metal remains in a finely divided state. Some of the stable double chlorides, especially the chloride of iridium, are soluble in water and are easily processed. With ores of different composition the method may vary. The processes worked out by refiners are usually guarded as trade secrets.

Smelting Methods

The older method for extracting platinum metals from their ores and concentrates is that in which the platiniferous material is smelted with lead oxide and fluxed. The platinum metals are taken up by the lead liberated in the operation and then reworked with an oxyhydrogen blowpipe to oxidize the lead, leaving a mixture of several resistant metals.

The smelting process for extracting platinum and related metals may be used for concentrating ore, metallurgical by-products, and other platiniferous substances on a large scale. It is useful for recovering very small amounts of these metals, and its accuracy and efficiency are on a par with fire assaying and recovery of small amounts of gold and silver. In large-scale platinum refining by smelting, lead oxide is substituted for high-grade lead ores. The platiniferous lead so obtained is

cast into ingots, allowed to cool, and then subjected to cupellation.

Solution Methods

The wet, or chemical, methods of recovering and refining the platinum metals are usually employed at the present time. Platinum ore responds to chemical treatment to a varying degree, depending on the metals present and the form of alloy or ore in which they exist. If platinum exists as the crude metal in dull grains with a 5 or 10 per cent admixture of other platinum metals, the acid treatment may be performed with little difficulty. Crude platinum of this sort is readily dissolved by hot aqua regia. Refining is relatively simple.

However, if the platinum metal consists mainly of osmium and iridium, e.g., the native alloy osmiridium, and only a small amount of platinum, solution with aqua regia may be a difficult problem. The bright grains of osmiridium are not immediately attacked by the aqua regia.

After the platinum is dissolved with aqua regia, ammonium chloride is added, and the platinum alone precipitates out as ammonium chloroplatinate. After drying, washing, and drying again, the ammonium chloroplatinate is heated in a magnesium oxide crucible or on a block of calcium oxide with an oxyacetylene flame, the compound being decomposed into gaseous ammonia and hydrogen chloride. The platinum is left behind in a spongy, unfused state. Spongy platinum can then be melted down to button form with the torch and further treated.

When ammonium chloride is added to the aqua regia solution, the platinum immediately precipitates out and may be quickly removed. If an excess of ammonium chloride is added to the mother liquor after the platinum is removed, the iridium will also precipitate out as ammonium chloroiridiate. The solution must remain undisturbed for some time, however, before all the iridium will precipitate out. Pure iridium is ob-

tained, like platinum, by calcination of the ammonium chloroiridiate in a magnesia crucible at a high temperature.

After the platinum and iridium have been removed, other members of the group may still be present in solution in small amounts. The careful addition of zinc shavings to the acid solution throws the remaining platinum metals out as a fine black precipitate called *first blacks*. Base metals, such as copper, are removed from the blacks by treating with sulfuric acid, although previous drying and roasting may be required.

Platinum-Blacks

The *blacks* are treated with aqua regia to obtain solution of the palladium, the traces of rhodium, and perhaps the small amount of platinum and iridium that have passed through the first treatment. The platinum, iridium, and rhodium are precipitated with ammonium chloride as in the first operation. The palladium is separated by metallic iron, forming a black mass, which may be fused down to a silvery button resembling platnium.

An insoluble residue may separate from the acid treatment, consisting mostly of rhodium and iridium. In this case, the residue is fused with barium oxide, and the fusion product treated with aqua regia. The rhodium and iridium will pass into solution. These metals may then be precipitated with ammonium chloride.

For the insoluble osmiridium residue that remains, zinc fusion is used, and the fusion product is treated with aqua regia. On steam distillation of the acid solution, the osmium passes over as osmium tetroxide and is collected under water. The residue from the distillation contains iridium and ruthenium, which may be separated with ammonium chloride by fractional precipitation. In precision work, where compounds and metals of a high degree of purity are required, several precipitations may be needed before complete separation is achieved.[8]

Platinum

Physical Properties

Platinum, the most important member of the platinum family, is a lustrous, bluish-white metal which crystallizes in the cubic system. The atomic weight of platinum is 195.2 and its specific gravity is 21.45. Pure platinum melts at 1773°C and boils at 4300°C. Platinum is a rare metal; it is only about one-hundredth as plentiful as gold.

Pure platinum is extremely ductile and rates as the most malleable metal after gold and silver. In tenacity it ranks next to iron, copper, and nickel. A wire 1.3 mm in diameter requires a load of almost 50 kg to break it, or 50 per cent more than is required for gold. Its specific heat is about the same as that of gold, being 0.03203 at room temperature. Platinum has a lower thermal conductivity than gold.

Platinum melts with difficulty in ordinary furnaces, but the metal may be fused easily in a high-frequency induction furnace, or by means of the oxyhydrogen flame. In melting platinum and many platinum alloys, a calcium oxide crucible is generally employed. Ordinary clay crucibles and clay refractories are not satisfactory. In preparing a crucible for fusion of a small amount of platinum into a button, a block of magnesia may be used, a cavity being hewed out in the center and the flame directed obliquely upon the metal.

Platinum is readily welded with the average equipment, electric or flame welding being satisfactory. The metal may be joined by heating to a bright red heat and hammering. Several solders are available for soldering platinum and its alloys. The nature of the solder is usually governed by the application to which the joint is to be put. Fine gold may be employed for soldering, and some solders of high silver content are also useful.

Workability

Platinum may be drawn into wire without using a hot die. In drawing platinum clad or filled platinum, which are composite structures of platinum on another metal, special precautions are required to insure good results. Pure platinum, because of its superior workability, may easily be spun and fabricated. When working platinum on the lathe or milling machine, or when preparing seamless tubing with a punch press, the metal acts somewhat like pure copper. The same general practice has been recommended for both metals.

Platinum and its alloys may be worked at bright red heat until they are thoroughly reduced, and then swaged, rolled, or drawn. After working platinum several times in a rolling machine, for example, the metal must be annealed by heating it to slightly over 1000° C. Higher temperatures are required if iridium is present, or if the alloy contains metals which radically alter the working properties. The physical properties of platinum alloys and other platinum metals will be discussed presently.

TABLE 37

PHYSICAL PROPERTIES OF PLATINUM

Property	*Value*
Specific gravity	21.45
Melting point	1773.5°C
Boiling point	4300 °C
Heat of fusion	27.18 cal
Specific heat at 18–100°C	0.0324 cal
Vapor pressure at 4180°K	760 mm
Volatility at 1300°C (Os=1000)	2
Specific resistance	11.8 microhms-cm³
Thermal conductivity at 18°C	0.166 cal/g
Moh hardness	4.3
Cathode sputtering (Pd=100)	40
Rigidity, cast	6.10 kg/mm²
Linear coefficient of expansion at 40°C	0.0899 x 10⁻⁴
Electric conductivity Cu=100	13.4%
Tensile strength (cast)	45,000 lb/in.²

The more important physical properties of platinum are given in table 37. These are frequently of utmost significance in specialized applications of this metal. Several books contain information on the physical properties of platinum and these should be referred to when data are required for highly specialized applications of this metal.[9]

Chemical Properties

At ordinary temperatures pure platinum is resistant to oxidation, and even at high temperatures it resists oxidation for short periods of time. However, it has been found that crucibles of platinum and platinum-iridium alloy tend to lose a little weight when subjected to extremely high temperatures for long periods of time. Pure platinum is not affected by many ordinary

TABLE 38

* Chemical Action on Platinum Metals

	Pt	*Pd*	*Rh*	*Ir*	*Os*	*Ru*
Acetic acid	−	−	−	−	−	−
Ammonium hydroxide	−	−	−	−	−	−
Aqua regia	+++	+++	−	−	−	−
Aqua regia, boiling	+++	+++	+	−	++	+
Bromine	−	++	−	−	−	−
Chlorine	−	++	−	−	−	−
Hydrochloric acid	−	+	−	−	−	−
Hydrofluoric acid	−	−	−	−	−	−
Nitric acid	−	++	−	−	++	−
Oxalic acid	−	−	−	−	−	−
Potassium bisulfate	+	++	++	−	+	+
Potassium hydroxide, aqueous	−	−	−	−	−	−
Potassium hydroxide, fused	+	+	+	+	++	++
Sodium carbonate, fused	+	+	+	+	+	+
Sodium hydroxide, aqueous	−	−	−	−	−	−
Sodium hydroxide, fused	+	+	+	+	++	++
Sulfuric acid, 20°C	−	−	−	−	−	−
Sulfuric acid, 100°C	−	+	+	−	−	−
Sulfuric acid, 250°C	+	++	+	−	+	−

* Unattacked = −; slightly attacked = +; moderately attacked = ++; and, strongly attacked = +++.

reagents, but bromine and chlorine attack it slightly when wet. Nitric, hydrochloric, and sulfuric acids do not affect platinum at ordinary temperatures, but sulfuric acid at 250°C corrodes it slightly.

Although platinum is not oxidized in the air at any temperature and is not attacked by any single acid, there are many substances which do affect it at comparatively low temperatures.[10] Heated platinum is affected by free sulfur arsenic, phosphorus, iodine, and selenium. Thus the fusion of sulfides, sulfates, and phosphates in the presence of reducing agents is detrimental to platinum crucibles and dishes. Organic substances containing phosphates, ferric chloride, alkaline cyanides, potassium nitrate, bromides, iodides, alkali hydroxides, alkaline earths, and especially barium and lithium hydroxides cause corrosion when ignited in platinum vessels in the air.

Many metals combine with platinum at red heat to form readily fusible alloys. Most harmful in this respect are lead, tin, zinc, bismuth, mercury, and antimony, or their compounds. The reduction of silicon dioxide by carbon in the presence of platinum forms silicon, which produces brittleness in the platinum. Platinum crucibles should not be heated in the inner cone of a Bunsen flame, as the carbon in this region reacts to form a carbide, causing general deterioration. A gray appearance is produced on platinum-ware heated in a Bunsen flame, which can be removed only by burnishing.

Ammonia attacks platinum, causing the surface to become darkened and less lustrous. It also produces coarse crystallinity on the surface. Highly carburetted gases and vapors cause the formation of carbides. Tellurium, like selenium, will attack platinum. The action of sulfur vapor is very slow; prolonged heating is needed to cause damage. Above 900°C magnesium pyrophosphate affects platinum. At very high temperatures borax and silicon dioxide affect it. Silver, gold, and copper, formed by reduction, may alloy with platinum. Peroxides affect the metal. Above 1200°C iron oxide is reduced and the

iron combines with the platinum. Above 1250°C lead and bismuth oxides act upon the metal.

The platinum alloys vary in their resistance to chemical reagents. When large amounts of palladium are present the alloy may very readily succumb to single acids. The presence of large amounts of iridium render the metal immune to attack from all but the most active substances, and in these cases the action is not rapid. Platinum-rhodium alloys are like palladium alloys in their resistance to reagents.

TABLE 39

* CHEMICAL ACTION ON PLATINUM ALLOYS

	90%–Pt 10%–Rh	*90%–Pt 10%–Ir*	*80%–Pt 20%–Ir*	*70%–Pt 30%–Ir*	*80%–Pt 20%–Pd*
Acetic acid	–	–	–	–	–
Ammonium hydroxide	–	–	–	–	–
Aqua regia	++	+	–	–	+++
Aqua regia, boiling	+++	++	+	–	+++
Bromine	–	–	–	–	+
Chlorine	–	–	–	+	+
Hydrochloric acid	–	–	–	–	+
Hydrofluoric acid	–	–	–	–	–
Nitric acid	–	–	–	–	+
Oxalic acid	–	–	–	–	–
Potassium bisulfate	+	+	+	+	+
Potassium hydroxide, aqueous	–	–	–	–	–
Potassium hydroxide, fused	+	+	+	+	+
Sodium carbonate, fused	+	+	+	+	+
Sodium hydroxide, aqueous	–	–	–	–	–
Sodium hydroxide, fused	+	+	+	+	+
Sulfuric acid	–	–	–	–	–

* Unattacked = –; slightly attacked = +; moderately attacked = ++; and, strongly attacked = +++.

Technology

Because of their superior properties, pure platinum and alloyed platinum find wide usage. Platinum is ideally adapted for use at high temperatures. A considerable amount of the annual platinum output goes into jewelry. Both physicists and

chemists have chosen platinum and platinum alloys for their standards of mass and length.

The development of the X-ray depended upon platinum in several ways: early X-ray tubes were made with platinum targets, and fluoroscopic screens were coated with barium platinocyanide or some similar salt. Vacuum tubes used in communication, medical therapeutics, and many other fields often employ small amounts of platinum.

Fortunately the supply of platinum is increasing. Usually, the metal can be reclaimed at almost face value long after the article into which it has been made has ceased to be useful. A great disadvantage of platinum, however, is its price. Although platinum is about 100 times as scarce as gold, its price has been close to that of gold during the decade 1931–1941.[12]

Platinum Ware [10]

One of the most important uses of platinum is in metal vessels used by the chemist and chemical engineer. Since pure platinum is somewhat soft for ordinary usage, a small amount of iridium is usually added to harden it and to impart other desirable properties. Because of its high melting point and the resistance to chemical agents, equipment made from this metal insures better results, purer products, and greater satisfaction in working with corrosive chemicals. Platinum employed as a crucible metal usually has 0.3 per cent iridium alloyed with it. However, at times it may require an iridium content of 10 per cent or more.

Many sizes and forms of platinum ware are on the market. Platinum Gooch crucibles, for example, are used in analytical chemistry. There are also platinum combustion boats, ignition vessels, incinerating pans, etc. Many official methods prescribed for chemical analysis specify that operations should be carried out in platinum vessels.

Much of the modern scientific equipment makes use of small amounts of platinum. Platinum electrodes are important

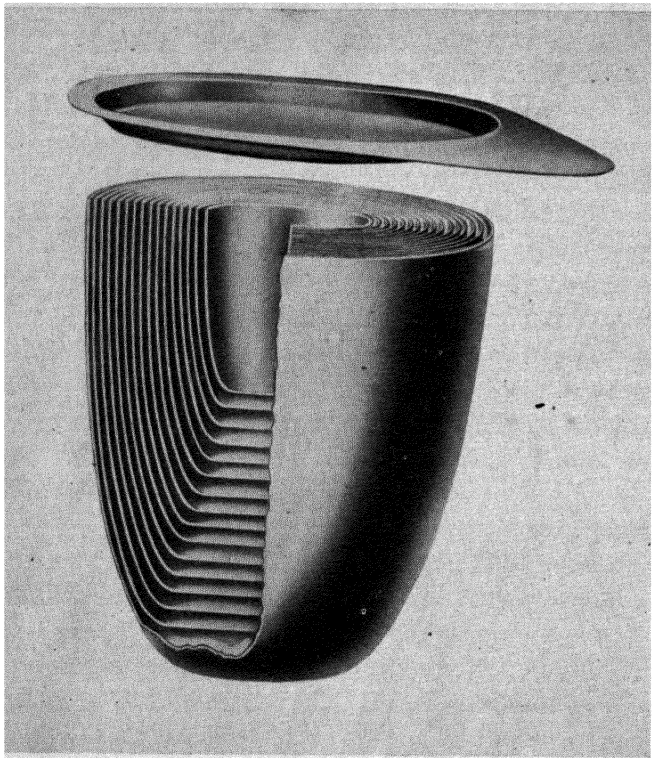

FIGURE 35
Crucibles of platinum alloy (courtesy of Baker & Co., Inc., Newark, N. J.).

in evacuated tubes when radiation is generated by high voltage electrical discharges. Since platinum has approximately the same coefficient of expansion as glass, it is sometimes used as a conductor and lead-in in glass vessels.* Much of the success

* Practically all of the small seals to soft glass for tungsten lamps, soft glass radio tubes, X-ray tubes, etc., have been made for many years with Fink's Dumet leading-in wire, a copper-clad nickel iron (U. S. Patent 1,498,908). Were we to return to platinum seals today there would not be enough platinum available in the world to take care of the many millions of glass seals.

achieved in physical and chemical investigations can be credited to platinum. Moissan, for example, isolated fluorine with the aid of platinum laboratory ware.

Industrial Equipment

Besides the small vessels employed by the chemist or physicist, there are large platinum retorts and special processing equipment used by the chemical engineer. As early as 1809 a London manufacturer constructed a platinum distillation apparatus for the concentration of sulfuric acid which weighed 424 ounces (13.2 kg). Later, much larger units were made by other manufacturers, and there is equipment in operation at present which weighs many pounds.

For processing gold, silver, and other metals, in which solution with nitric acid is required, large platinum vessels have played an important role, but stainless steel has largely supplanted them. The usefulness of platinum and its alloys for tubing, valves, and syphons for the safe and efficient handling of corrosive liquids and gases is well known. Platinum is widely employed in measuring and recording equipment in the manufacturing plan and laboratory.

It has been pointed out that a material increase in the world's production of platinum metals in recent years is due principally to improvements in metallurgical processes. The refining of nickel and copper ores and other electrolytic processes yield small amounts of platinum, palladium, ruthenium, rhodium, and iridium, which are invariably present as impurities.

In preparing artificial fabrics like rayon, a viscose solution is usually extruded through fine apertures. The economy and efficiency of platinum spinnerets are well illustrated in the case of rayon. An alloy of this metal withstands corrosion and abrasion, and an average jet will produce approximately 4000 lb of yarn at a cost of less than 0.01 cent per pound of yarn in terms of metal. Likewise, in the production of glass and plastic wool, platinum and its alloys are used for feeder dies or bush-

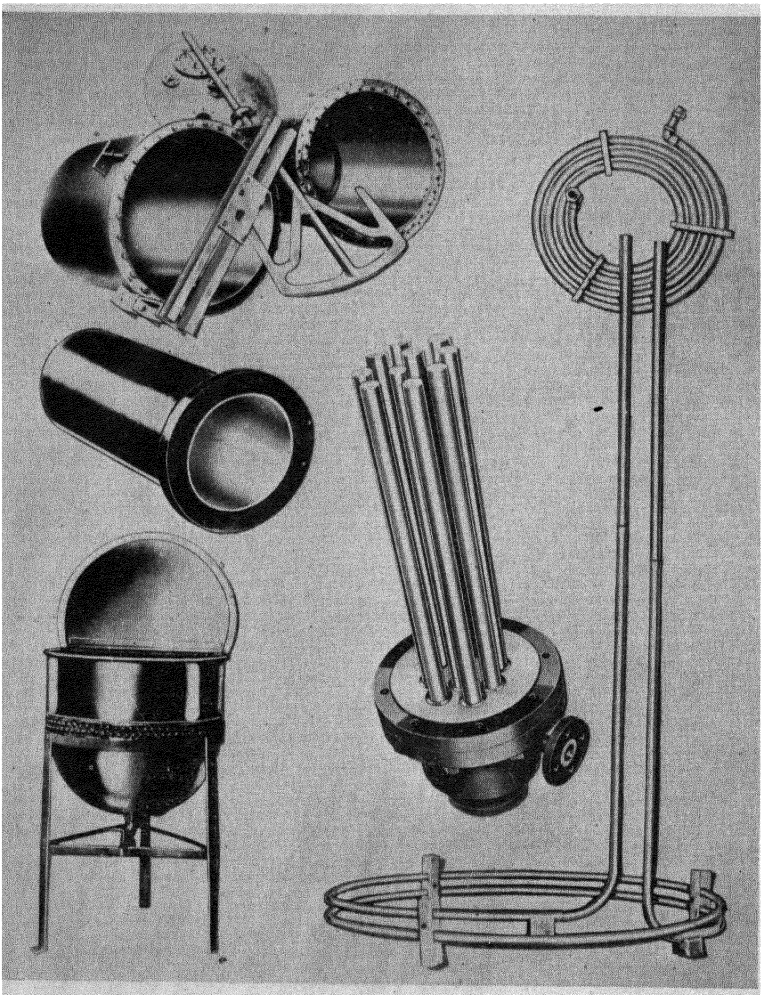

FIGURE 36

Platinum-clad industrial equipment (courtesy of Baker & Co., Inc., Newark, N. J.).

Pure platinum or an alloy of platinum is used for this purpose, which is so securely bonded to a base metal that the clad composite can be fabricated.

jngs through which the glass or plastic flows in a steady stream and is carried onward as a wool-like mass of fine fibers.

Glass insulators for the brass bases of electric incandescent

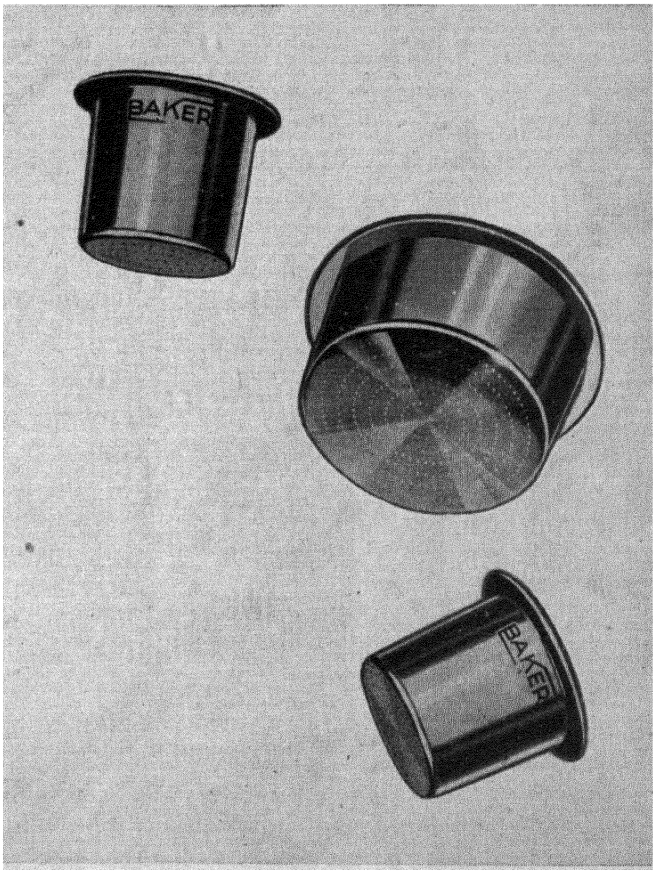

FIGURE 37

Platinum spinnerets used in the synthetic fiber industry (courtesy of Baker & Co., Inc., Newark, N. J.).

Tooling the holes of a spinneret is a precision job, individual holes sometimes measuring 0.002 in., and a single spinneret having as many as 5,000 holes.

lamps are made with platinum feeder dies to insure accurate delivery of the glass for the bases. Platinum dies have permitted the smooth and uninterrupted production of 38,000,000 such bases per die before salvage of the die is required. This is contrasted to a ceramic die in which no more than 2,000,000 bases were produced with no salvage of the die possible.

Single crystals of lithium fluoride weighing as much as 24 lb can be made in platinum crucibles. These are important in optical work. Platinum is the only metal which will withstand the corrosive action of molten salts without contamination of the finished products. Very large crystals of potassium bromide, rock salt, and sodium nitrate have been prepared by melting the salt in a large platinum crucible and allowing crystallization to take place.

Catalysis

Platinum and the platinum metals have been involved in practically all catalytic operations, both in the laboratory and in industry. Many food products, fuels, and other substances employed in our everyday life could not have been possible without the use of platinum.

Platinum metals work well at high temperatures where many base metal catalysts fail.[13] Platinum catalysts enhance a great number of chemical reactions, both organic and inorganic. At low temperatures these catalysts also excel in ease of operation, economy and ruggedness.

Probably one of the first important applications of platinum catalysts was to the manufacture of sulfuric acid by a process invented by Messel in 1875, known as the contact process. In this method the sulfur is burned in air to form sulfur dioxide, and upon passing the sulfur dioxide and oxygen over platinized asbestos, sulfur trioxide is formed. When water is added, sulfuric acid results. Combination begins at 300°C.

Nitric acid, another important commercial chemical product, may be produced by the catalytic action of platinum. Hydro-

genations, dehydrogenations, halogenations, and dehalogenations may be brought about by the action of platinum.

For the synthesis of hydrocarbons of high molecular weight, platinum-group alloys can serve as catalysts. To prepare these hydrocarbons, only carbon monoxide and hydrogen are required. For introducing the hydroxyl group into the substances, osmium tetroxide has been found valuable.

In catalysis at high temperatures, pure platinum gauze may be used, or the platinum may be alloyed with from 5 to 10 per cent rhodium. The catalyst carriers which have been devised for the hydrogenation of such liquids as cottonseed oil, at ordinary pressure and room temperature, include gelatin colloid, zinc carbonate, and calcium carbonate. They contain varying amounts of platinum, ranging up to about 10 per cent. Platinum-rhodium gauze and palladium are frequently used as catalysts, especially in hydrogenations.

Jewelry

About one-third to one-half of the present output of platinum is used in jewelry.[14] The use of platinum and its alloys in this industry is of comparatively recent origin, having developed in the past forty years or so. Because of its beauty, mechanical strength, and durability, platinum has come to supplant gold and silver in many of the expensive and elaborate pieces of jewelry. Pure platinum, like gold, is rarely used in jewelry because it is too soft; a small amount of iridium or ruthenium is alloyed with it.

At one time the practice of alloying palladium with platinum for use in jewelry, and selling the article as pure platinum, caused much litigation. Palladium gives some desirable properties to platinum. The alloy is still used in the jewelry trade, but not with fraudulent intent, as was the case when the price of palladium was lower than that of platinum. A number of laws have been passed to govern the marking and sale of platinum-palladium jewelry alloys.

With the increased demands for platinum during wartime, for use as catalysts in making acids and processing vital war materials, the supply of this metal for jewelry has dropped considerably. This is offset to a certain extent by using the other platinum metals, notably palladium, whose applications to industry are not so extensive but which are good substitutes in jewelry.

High Temperature Work

Because of the high fusing points of platinum and its alloys, they serve as furnace windings in industrial electric furnaces, in ordinary atmosphere, at temperatures well over 1200°C. This accounts for the fact that the platinum metals are often called refractory.

Special insulating substances must be employed in platinum resistor furnaces to insure long usage. Usually platinum wire is used in very small furnaces, such as laboratory furnaces, but for larger furnaces, platinum ribbon is better. Magnesia, lime, and alumina have been employed as refractories. Recently, the oxides of some of the rare earths, such as lanthanum, have been introduced as refractories.

Electric Lamps

At present the use of platinum-osmium and allied metals in filament lamps is very rare. Platinum and osmium filament lamps, however, were in vogue in the early days of incandescent lighting. The first practical metal filament contained osmium. This fact is perpetuated in the trade name *Osram*, a contraction of osmium and wolfram, which is still a trademark of certain tungsten lamp manufacturers. Osmium has not been used for filament since 1905. Osmium filaments were replaced by tantalum, and in 1907 these were replaced by tungsten. For some time platinum was the only metal available for lamp seals, but this wasteful use of platinum has now been obviated by the introduction of Fink's Dumet copper-clad nickel-iron wire, which is much cheaper.

The discovery and development of the incandescent electric lamp can be attributed partly to the refractory qualities of platinum and allied metals. In the summer of 1878, Edison investigated the platinum metals as filament material.

Platinum metal filaments were not entirely satisfactory. However, Edison continued his experiments until about April, 1879. He did discover that if he introduced a piece of platinum wire into a glass envelope, completely sealed and highly exhausted, and passed a current through the platinum wire in vacuum, the wire would give off light equal to 25 candlepower without melting.

Platinum Plating

In platinum plating there are two aspects to consider. In the first place, the platinum to be deposited on any subject is very often present in solution along with other substances which insure optimum operating conditions. Usually this platinum may be replenished by adding more of the platiniferous compound. However, if plating depends upon passage of an electric current through electrodes and solution, as it nearly always does, one of the electrodes is usually pure platinum. In most processes, the anode is platinum and the object to be plated forms the cathode. The platinum anode may change during the deposition, although in some processes it remains unaffected, because it does not provide any of the metal to the coating.

Platinum plating was developed in about 1883 by Pilet, who was granted a French patent on his process. Many years later an investigator named Pfanhauser described a method of platinum plating which was based on the older one by Pilet. Pfanhauser's platinum bath is prepared as follows:

Water	1 l
Diammonium phosphate	20 g
Disodium phosphate	100 g
Chloroplatinic acid	4 g

The platinum bath, using platinum anodes, is intended mainly for flash plating. The solution is prepared by boiling until a pale yellow color is produced, indicating the formation of complex platinum amminophosphates. In plating, the solution is operated close to the boiling point, at 3 to 4 volts, with a current density of about 1 ampere per square decimeter. Bright flash deposits are obtained in from 30 to 120 seconds, after which the deposit becomes somewhat cloudy and gray. Heavier plate can be obtained by increasing the metal concentration and the current density. The metal content is maintained by additions of chloroplatinic acid.[15]

Another platinum plating bath, of the platinum diammino type, has been described.[16] It consists of the following:

Ammonium nitrate	100 g/l
Sodium nitrite	10 g/l
Platinum diamminonitrite	16.5 g/l
Ammonium hydroxide	50 g/l

Before preparing and using this plating bath, the descriptions given in the original patent or reference should be consulted.

The platinum metals can be plated on glass. Bright silvery, blackish, or gray films may be employed in optics, for coating lenses and large telescope mirrors, which require permanency and high reflectivity. Since rhodium has an extremely high reflectivity and is easily plated, extended use for this metal has been found for searchlight reflectors. Platinum, iridium, palladium, osmium, ruthenium, as well as rhodium, have all been plated on glass and similar substances with good results.

Black osmium deposited on a base of bright platinum on glass has proved of value in the study of glass oxygen electrodes.[17] Burning and sputtering may be used instead of electrolytic deposition.

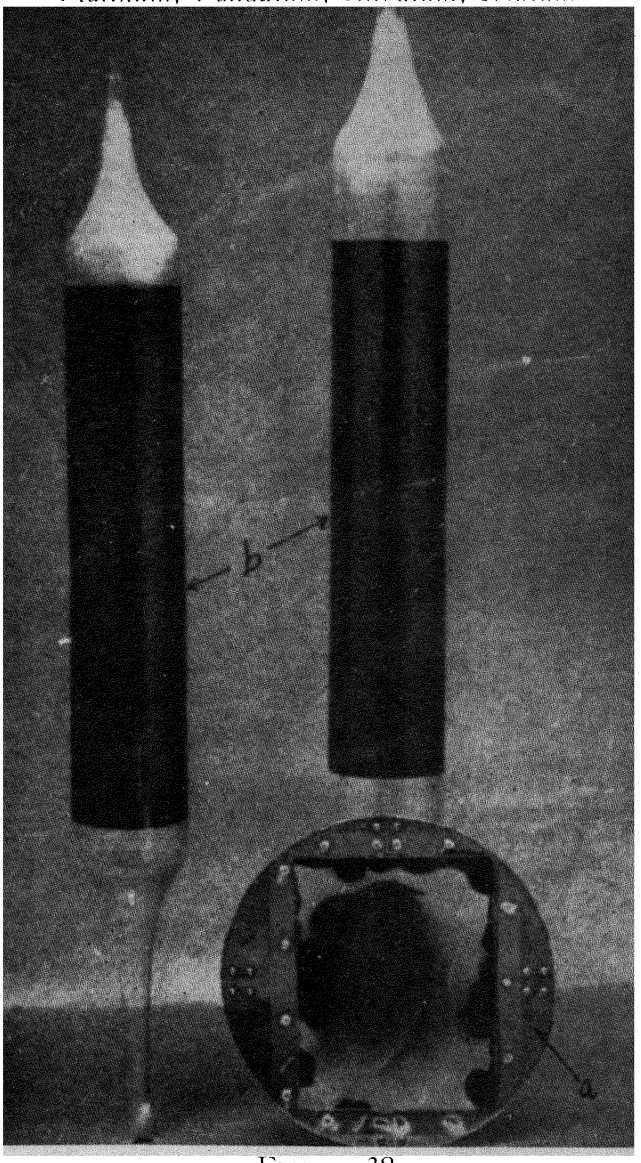

FIGURE 38

Metal lusters of platinum, silver and gold [S. F. Essig, *Trans. Electrochem. Soc.*, **87** (1945)].

a Platinum-gold luster on mica.

b Silver-bearing platinum-gold luster inside two glass tubes.

Fluorescent Screens [18]

Many double salts of platinum are brilliantly fluorescent under X-rays, ultraviolet light, and cathode rays. They have found use in medicine, science and industry for fluoroscopic screens. In 1896 Edison studied about 1800 chemical compounds looking for substances suitable for use in fluoroscopic screens. Although he found several compounds with excellent properties, a series of double platinum salts were eventually employed as the active substances on fluorescent screens.

The highly fluorescent platinum compounds are the double salts of alkaline earth cyanides. Platinous barium cyanide was first used, but later studies showed that several others could be employed. Platinous lithium cyanide and platinous thorium cyanide were also used, but the compound of brightest luminescence was platinous lithium rubidium cyanide. However, this compound was not used to any great extent because of its high cost.

Platinous barium cyanide forms large dichroic crystals, containing 38.38 per cent platinum. They are soluble in water. The substance is yellowish-green by transmitted light and bluish-violet in reflected light. Under X-rays and ultraviolet light, a brilliant yellowish-green fluorescence is produced. Platinous lithium rubidium cyanide consists of greenish-yellow crystals or needles which are soluble in water.

Details of the manufacture of platinum compounds for roentgenography and fluoroscopy are difficult to obtain. In general, however, mol equivalents of platinous cyanide and the alkaline earth cyanide are crystallized together from hot water to form a fluorescent residue. For example, platinous barium cyanide consists of 48.6 per cent platinous cyanide, 37.23 per cent barium cyanide, and 14.17 per cent water when it occurs with four molecules of water of crystallization. In preparing the screen, either the crystals or an aqueous solution of the platinous barium cyanide is mixed with an adhesive and painted on cardboard, paper, or wood, and carefully dried.

Other Uses of Platinum

Of the hundreds of outstanding applications of platinum and its alloys, the most interesting is the use of a bar of platinum-iridium alloy for the standard meter, the Étalon, made in 1870 by Johnson and Matthey & Company for the Comité International des Poids et Mesures. After exhaustive tests it was found that an alloy of 90 per cent platinum and 10 per cent iridium served the purpose well. Subsequently all standard meters and later the mass standard, the kilogram, were supplied by this firm, and the amount of platinum used in the manufacture of these standards was about 250 kg, or nearly 670 lb troy.

Platinum electrodes are universally used in electrolytic procedure both for analysis and for synthesis on a commercial scale. Platinum finds use in tips for surgical implements and cauteries, as well as for screws and wire used in bone work and suturing.

Platinum contacts find wide use in electrical apparatus, sensitive thermocouples and relays. Surveying instruments, analytical balances, sextants, and numerous other scientific instruments use platinum.

At one time platinum found use in photographic work, when platinum prints were in vogue. However, with the tremendous advances in the field of photography, this metal has almost been abandoned. Bimetallic thermoflex elements and electrodes for pH and conductivity control also employ platinum.

Platinum alloyed with gold and various other members of the platinum group of metals finds wide use in the field of dentistry. High karatage gold is comparatively soft, but when alloyed with even a small amount of platinum its resistance to attrition is greatly increased. Platinum-containing alloys are frequently used in inlays in teeth which must support bridgework. Thin platinum foil is used in the manufacture of porcelain jacket crowns. The coefficient of expansion of platinum (8.99×10^{-6}) is near that of fused porcelain (8.3×10^{-6}), hence this metal has been widely used in the manufacture of

porcelain facings and crowns, where metal pins or posts must be baked into the ceramic. Owing to the introduction of various plastic porcelains, less platinum is being used in dentistry. A great many platinum alloys have been used in dentistry.[19]

Analysis

In detecting platinum, 5 g of the sample are dissolved in aqua regia in a small porcelain vessel and evaporated to dryness on a water bath. The residue is gently heated until every trace of nitric acid has been removed and the solid is completely dissolved in water. To the clear solution a few drops of potassium iodide solution are added. After the platinum iodide which has formed dissolves, a deep-reddish solution results. The addition of a few drops of acid to the colored solution hastens the appearance of the color, and heating causes it to disappear. Hydrogen sulfide, sodium sulfite, sodium thiosulfate, sulfurous acid, and mercuric chloride also remove the color.

For the quantitative estimation of platinum, according to Ohly, 2 to 5 g of the ore are dissolved with aqua regia, evaporated to dryness, and dissolved in hydrochloric acid and hot water. After filtering and washing, hydrogen sulfide is introduced into the solution. After standing overnight, the sulfide is filtered off, washed with hydrogen sulfide water, and dissolved in a small amount of aqua regia.

The solution is diluted and any sulfur that separates out is removed by filtration. The acid solution is added to a saturated solution of ammonium chloride and sufficient alcohol is added to render the precipitation of ammonium chloroplatinate complete. After filtering, the precipitate is washed with water containing a small amount of ammonium chloride and alcohol. The precipitate is ignited in a covered crucible until the ammonia and chlorine have been driven off. Finally, the crucible is partly opened and the carbonaceous matter is burned off. The

cooled residue is weighed as metallic platinum. The precipitate may contain traces of double salts of other platinum metals, which should be removed and analyzed.

To recover the platinum from laboratory residues, a neutral solution containing the platinum is heated to boiling, and a saturated solution of sodium carbonate and glycerin is added. All the platinum present will precipitate out. After filtering, washing, and drying, the platinum is ignited and weighed as the metal. It is necessary that sodium carbonate be added in excess. If iron or other metals are present, acid digestion may be employed to remove them. Paper residues must be burned first and incinerated in the muffle before they are digested with aqua regia and the resulting solution treated with ammonium chloride.

Platinum and trivalent gold salts in solution produce a blue precipitate or turbidity when added to a solution of 1 g of benzidine in 10 cc acetic acid and 50 cc of water.[20]

The addition of 5 drops of a 2 per cent alcoholic solution of phenylthio-carbamide to 1 cc of solution gives a yellow precipitate or turbidity with auric, platinic, and palladous ions. In order that the test be satisfactory, mercury, copper, and silver must be removed, since they are also reactive. Mercury gives a grayish, copper a yellowish, and silver a brownish turbidity.[21]

The addition of stannous chloride solution to a platiniferous solution gives rise to a red color which can be extracted with ether or ethyl acetate. When the extracted portion is diluted with water, the red solution deposits a chocolate brown precipitate. On heating the red solution the color changes from dark red to black.[22]

Thompson, Beamish, and Scott [23] have developed several reactions for platinum. In one, a 40 per cent solution of stannous chloride in hydrochloric acid gives an orange or yellow color with platinic ions. A faint yellow coloration forms with as little as 10 gammas per cc. Palladium and gold must be removed.

In a second test, a drop of 10 per cent potassium iodide is

added to platinum in hydrochloric acid, producing a red-brown precipitate. A distinct reaction is given with 2 gammas of platinum per cc. Palladium and gold must be removed.

Platinum forms bronze or blue crystals with dimethylglyoxime. When studied microscopically, they are found to be prismatic and dichroic.

Separation of Platinum Metals

The separation of platinum metals is often beset with many difficulties. Leidie and Quennessen [24] have proposed a method which was formerly used a great deal for platinum metal ores. At present the same method is used in many laboratories with minor modifications. The scheme for separation is as follows:

The finely divided metals are mixed with at least 5 to 6 times their weight of sodium peroxide and heated gently in a nickel crucible. After treating with water, the mixture is filtered. The residue contains nickel, platinum and rhodium as insoluble compounds. It is treated with hot hydrochloric acid, filtered, and the excess acid is evaporated. Sodium nitrite is added and the solution made neutral with sodium carbonate. After boiling, the solution is filtered, the nickel remaining as a precipitate. The filtrate contains platinum and rhodium. An excess of hydrochloric acid is added and the solution is evaporated to dryness. Water is added and ammonium chloride mixed in with the solution. The platinum is precipitated as the chloroplatinate, but the rhodium remains in solution as the reddish double chloride.

The filtrate from the first operation contains soluble sodium salts of osmium, ruthenium, iridium, and palladium. A yellow solution indicates the presence of osmium, ruthenium, and/or palladium; a blue solution indicates iridium. A colorless solution indicates the absence of all these metals. If the solution is colored yellow, chlorine is passed through it, and it is heated in a distillation apparatus. The distillate, when treated with

ammonium sulfide, gives a black precipitate if either osmium or ruthenium is present. If osmium is present, a violet osmate will form from heating the solution with potassium nitrate.

If ruthenium is present, a black precipitate of ruthenium is formed by adding alcoholic potassium hydroxide in the cold. However, if the distillate is blue instead of yellow, it is neutralized with hydrochloric acid and evaporated in the presence of ammonium hydroxide and potassium chloride. Black crystals of potassium chloriridate form if iridium is present.

The residue from the distillation will contain all the palladium that may have been present. This is neutralized with hydrochloric acid and evaporated with ammonium hydroxide and potassium chloride. If palladium is present, red crystals of potassium chloropalladate will form.

Palladium

Physical Properties

Pure palladium is a lustrous, silvery-white metal belonging to the lighter group of platinum metals. Next to platinum, palladium is the most abundant of the platinum metals. It is much lighter than both gold and platinum, having a specific gravity of 12. Palladium is the most fusible of the platinum metals, requiring a temperature of only 1554°C to bring it into a liquid state.

Palladium metal has several unusual properties. It is softer than platinum and takes a high polish. In general, the workability of palladium is comparable to that of some gold alloys, and slightly less than that of silver. Palladium can be swaged, hammered into thin foil and drawn into fine wire.

Palladium resembles steel in hardness. It can be welded more easily than platinum. It can be fused with difficulty in an ordinary gas muffle furnace, but oxyacetylene and oxyhydrogen torches are frequently employed to work it. When palladium is

fused into a button, it absorbs oxygen from the air and evolves it on cooling, showing a tendency to *sprout* like silver. Palladium does not tarnish on exposure and resists the action of sulfur-derived gases.

TABLE 40

PHYSICAL PROPERTIES OF PALLADIUM

Property	*Value*
Specific gravity	12
Melting point	1554°C
Boiling point	2200°C
Specific heat	0.053 cal
Volatility at 1300°C (Os = 1000)	6
Thermal conductivity at 18°C	0.168 cal/g
Electrical conductivity at 0°C	10.7 microhm-cm
Brinell hardness	109

Gas Occlusion

An outstanding property of palladium is its capacity to absorb hydrogen. Recent research, however, has shown that this characteristic depends upon a chemical reaction. Absorption takes place at ordinary temperatures and is accelerated by a rise in temperature. The physical structure of the metal affects the absorption. Freshly ignited palladium foil, for example, takes up more than 370 volumes of hydrogen at room temperature, and when heated to 100°C about 650 volumes of gas are absorbed. Specimens have been prepared which retain more than 980 volumes of hydrogen at 100°C. Spongy palladium and finely divided palladium known as *palladium-black* both have an enormous capacity for holding hydrogen.

Hydrogen combines with palladium to form palladium hydride, Pd_2H, a compound which exists in solid solution in the palladium metal remaining when the reaction with hydrogen is incomplete. The reaction of hydrogen with palladium is important in chemical processing. Palladium and palladium hydride cause the decomposition of hydrocarbons at tempera-

tures far below those which would otherwise decompose hydrocarbons. When heated to several hundred degrees in contact with a hydrocarbon, the palladium swells, and carbon is liberated from the hydrocarbon. Palladium hydride is one of the most powerful reducing agents known, and it may be used in organic chemistry and in pharmaceutical manufacture.

Finely divided sponge-palladium and palladium-black act as a catalyst. For catalytic applications, palladium may be prepared in the spongy form by ignition of a comparatively unstable compound. Metallic palladium may be precipitated on asbestos and used as a catalyst. This preparation is called palladized asbestos.

Chemical Properties

Although palladium does not tarnish in air or in sulfur-derived gases, acid vapors and halogens, especially chlorine, exert a strong effect upon it. Because of this property palladium does not find extensive application as a substitute for platinum in crucibles and alloys, which must be highly resistant to chemical agents. Pure palladium dissolves easily in cold and dilute nitric acid. If an alloy is prepared with the greater part consisting of platinum, nitric acid will not attack it. When palladium is heated strongly in the oxyhydrogen flame, a greenish vapor may be emitted.

Compounds

Black palladous sulfide is formed when hydrogen sulfide or ammonium polysulfide is added to solutions containing palladium. The addition of acid, particularly hot hydrochloric acid or aqua regia, causes solution of the precipitate.

In slightly acid solutions containing palladium, the addition of water will precipitate a brownish, insoluble hydroxide. It is also precipitated by soluble carbonates. Palladous cyanide is yellowish-white and gelatinous when freshly precipitated. The addition of potassium cyanide or ammonium hydroxide will dissolve it.

Ammonium chloride does not precipitate palladous salts, as it does platinum and iridium salts. A double salt is precipitated, however, when potassium chloride is added to palladic solutions. Palladous salts may readily be separated from platinum by precipitation of the platinum with NH_4Cl. Potassium palladous chloride is brownish-red and insoluble in absolute methanol, although soluble in water. A number of chemical agents reduce palladous salts to the metallic state, e.g., sulfurous acid, phosphorus acid, formic acid, potassium nitrate, zinc and iron. Methanol and ethanol may exhibit the same action. This is the method for making palladium-asbestos.

Since palladium combines with the halogens and platinum does not, a simple spot test may be employed to distinguish between the two. When palladium is spotted with an iodine solution, a darkened region forms; platinum does not blacken with iodine. Palladous iodide, PdI_2, is precipitated as a black insoluble powder when potassium iodide is added to solutions of palladous chloride. Palladous chloride is prepared by simultaneous action of hydrochloric acid and chlorine upon palladium. The solution deposits brownish-red crystals of the dihydrate upon evaporation in a vacuum. When they are warmed, the anhydrous salt is formed. Palladous iodide is important because the reaction for preparing it is sometimes used for the separation of iodine from the other halogens, since the other halogen salts of palladium are soluble.[25]

Recovery from Palladiferous Ores

To recover palladium from platinum ores, the palladiferous material is dissolved in aqua regia and the insoluble residue filtered off. The acid filtrate is then treated with an excess of ammonium chloride and ethanol. The platinum and iridium are precipitated as ammonium chloro compounds and the palladous salt remains in solution. After the precipitate settles, the liquid is filtered and ammonium chloride and alcohol solution added to insure removal of all platinum and iridium by

filtering again if necessary. The filtrate is treated with mercuric cyanide to precipitate the palladium as the insoluble cyanide. Pure palladium metal is obtained by carefully igniting this compound.

Analysis

On boiling a palladous chloride solution, which has been acidified with hydrochloric acid, with a solution of α-nitroso-β-naphthol in acetic acid, a red voluminous precipitate of palladium complex forms.[26]

In the Tananaev-Dolgov test for gold, platinum, and palladium, several methods can be employed. Palladium can be detected by wetting filter paper with a drop of saturated thallium nitrate solution and auric chloride solution, then adding the solution to be tested. If the spot darkens, at least 0.35 gamma of palladium is present.[27]

Palladium can also be detected by placing a drop of mercuric cyanide solution on a filter paper, then applying the solution to be tested, followed by another drop of the cyanide reagent, and washing off the excess with water. A half drop of stannous chloride solution is then dropped on the spot. A rose-yellow coloration at the center indicates palladium and a yellow color at the outer edge shows the presence of platinum. A half-drop of benzidine solution is then dropped on the spot. A blue color at the periphery of the spot indicates the presence of gold.

A reagent for the quantitative determination of palladium and cobalt has been developed by Mayr. It consists of a filtered solution of 2 g of α-nitro-β-naphthol in 110 cc of glacial acetic acid and 100 cc of water.[28]

A microchemical test for palladium consists of adding sodium nitrite and an excess of ammonium hydroxide or sodium hydroxide to the solution to be tested. Large, colored rhomboidal crystals form.[29]

A test for palladium consists of adding to the solution to be tested an equal volume of a reagent made by dissolving 1 g

of *p*-amidoacetophenone in 40 cc with water. If palladium is present, a turbidity or voluminous yellow precipitate will be noted. The test is specific for palladium. Five gammas of the metal will give a reaction.[30]

A convenient spot test for palladium is made by using a reagent of *p*-dimethylaminobenzylidene rhodanine, with which the metal produces an insoluble precipitate. Silver, gold, copper, and platinum react similarly. The procedure is to place a drop of the solution to be tested on filter paper saturated with the reagent. Palladium reacts immediately whereas the others require a little time to develop the characteristic violet-red coloration. As little as 5 gammas of palladium per cc gives a violet ring.[31]

A similar test consists of using the same organic reagent, but dissolving 0.3 g of the solid in 100 cc of acetone. Palladium gives a flocculant red-violet precipitate which is also formed by gold and silver.[32]

On passing a stream of carbon monoxide through a boiling acidic solution containing palladium and phosphomolybdic acid, a blue to green coloration is produced in only a few minutes. Gold, mercury, and ferrous iron decrease the sensitivity, although 0.25 gamma of palladium per cubic centimeter of solution is claimed to be detectable by Feigl, the originator of the test.[33]

Palladium and gold are detected by adding a mixture of naphthylamine and ferric chloride to the solution to be tested. A blue coloration or red-violet precipitate forms with auric chloride and palladic chloride.[34]

Technology

Palladium is the chief rival of platinum in alloys for dentistry, jewelry, and catalysis. In fact, palladium imparts to some alloys properties which are much more desirable than those imparted by platinum. In a few cases palladium is a better catalyst than platinum.

Palladium chloride finds use in the detection and estimation of carbon monoxide in mines and garages. Very fine photographic effects are obtained by toning with palladium compounds. Palladium prints have held an interest for photographers for many years. Non-tarnishing palladium foil is used in place of silver foil to decorate glass and leather.

Palladium Catalysts

Palladium oxide (Adam's catalyst), prepared in the same manner as platinum oxide, is much used in hydrogenation. Carriers of various kinds may be employed as a base for colloidal palladium. The number of reactions catalyzed by palladium is surprisingly large. They include oxidation, chlorination, reduction, isomerization, polymerization, and synthesis, but the most notable reactions are the hydrogenation of oils and other organic substances.[45]

There are at least four or five hundred patents dealing with the catalytic properties of palladium. Baker Colloid 46 is an example of a palladium catalyst. It is a black aqueous solution containing 0.5 g/l of palladium. The metal in this solution is very uniformly and finely dispersed. The catalyst is unusually stable and can be used in neutral, acid, or alkaline solutions. Its activity is almost unaffected by the pH of the solution.

The success of this palladium catalyst depends on the size of the particles and the presence of a protective colloid which actually enhances the catalytic activity.

This palladium catalyst is very versatile. It can be employed in the hydrogenation of nitro groups, unsaturated carbon groups, aldehydes, ketones, and many other organic compounds. It is important in the production of isoprene by the hydrogenation of acetylenic alcohols.

Its activity can be illustrated by an experiment in which 1 cc of benzaldehyde is dissolved in 50 cc of denatured alcohol and 30 cc of water and 20 cc of the Baker palladium colloid are added. In 5 minutes, 240 cc of hydrogen are absorbed, and the

reaction is completed in 10 minutes giving benzyl alcohol as an end product.

Some interesting applications of palladium as a catalyst are found in cigarette lighters, foot warmers, etc. Usually the palladium is just one of a number of platinum metal catalysts on a base. A low-kindling-temperature solvent, such as methanol, bursts into flame when its vapors are played against this catalyst at ordinary temperatures in the presence of sufficient oxygen.

Palladium catalysts find application in cracking petroleum, in gas analysis, in the production of hydrocyanic acid from ammonia and acetylene,[36] and in the production of alkaline earth formates by the action of carbon monoxide on alkaline earth hydroxides.[37]

Palladium is a favored catalyst in hydrogenations where the product must be of high purity, e.g., in the manufacture of vitamins. There are numerous patents dealing with palladium catalysis in the preparation of various organic compounds, representative processes including the following: reaction of a mixture of acetylene and methane to give propylene; reaction of ammonia and acetylene to give pyridine bases; the hydration of olefins; preparation of the anhydrides of lower fatty acids; polymerization of petroleum hydrocarbons; reaction of unsaturated hydrocarbons with carbon monoxide; manufacture of ethyl alcohol from ethylene or acetylene; and, the conversion of olefines into alcohols.

The purification of rare inert gases is accomplished by using palladium catalysts. The removal of impure gases from krypton and xenon is achieved by passing them over a carrier of silicon and silicon dioxide. Pure hydrogen can be produced from phosphorus and steam by using a palladium catalyst.[38]

Palladium Alloys

Due to the shortage of certain metals during wartime, alloys employing platinum metals other than platinum itself have

gained favor. Palladium-gold is an alloy used by jewelry makers as a substitute for many of the gold alloys, which are difficult to obtain. Palladium-gold alloy contains about 19 parts gold and 5 parts palladium. It is almost as white as platinum and is easily worked, although it is a little soft. The alloy is non-tarnishing and has the rich finish required for jewelry.

Such alloys may be made from palladium with gold and/or a small amount of nickel to improve wearing properties and durability.

Palladium Plating

Palladium is being electrodeposited on an extensive commercial scale.[39] Pilet [40] patented a palladium plating bath in 1884. The Pilet bath is similar to the platinum bath developed by the same investigator one year previously.

Palladous chloride	3.7 g/l
Disodium phosphate	100.0 g/l
Diammonium phosphate	20.0 g/l
Benzoic acid	2.5 g/l

The solution is boiled until the dark red color changes to yellow, indicating that a complex has been formed. A temperature of 50°C is employed and a current density of 0.2 to 0.3 amperes per square decimeter used.

This bath is not very satisfactory, since the deposit remains bright for only a short time, and after the metal has been depleted, a dull plate forms. To raise the concentration of the metal, palladous chloride must be added and the entire solution boiled again. Palladium or platinum anodes are employed without damage to either. Palladium can be flashed directly on many metals, although a nickel undercoating is required for zinc, tin and lead alloys. When the pH is kept at 7.0 by adding

ammonium hydroxide, better results are obtained, and heavier coatings may be obtained by increasing the metal concentration.

Iridium

Physical Properties

Pure iridium resembles the other metals of the platinum group, being a lustrous, steel-white metal. It is intermediate in the heavy group of platinum metals. Iridium has a specific gravity of 22.4 and melts at 2350°C. It is one of the most dense substances known and has a very complex chemistry.

Iridium is harder than most steels, and, like many hard substances, it is also brittle. When heated, however, it becomes moderately malleable, and when alloyed with platinum, forms a metal which is hard, elastic, malleable and ductile. The platinum-iridium alloys are much less fusible than platinum. When the iridium content exceeds 20 per cent, the workability decreases.

The specific heat of iridium is 0.032 and its coefficient of linear expansion is less than that of platinum. When iridium is fused with phosphorus, a malleable compound is formed which is somewhat like phosphorus-copper. However, the phosphorus-iridium compound is not very stable at high temperatures; when heated to redness it decomposes. The phosphorus may be removed if an alkaline earth oxide is present.

TABLE 41

Physical Properties of Iridium

Property	*Value*
Specific gravity	22.4
Melting point	2350°C
Boiling point	4900°C
Volatility at 1300°C (Os = 1000)	60
Thermal conductivity at 18°C	0.141 cal
Electrical resistivity at 0°C	6.08 microhm-cm
Moh hardness	6.5

When iridium is alloyed with platinum, the product has properties superior to those of either metal. Platinum-iridium is employed for high temperature thermocouples and in standards of weight and length.

Chemical Properties

Iridium is insoluble in single acids, although there are one or two exceptions to this rule. Iridium is resistant to aqua regia, but if alloyed with a large enough amount of platinum, a reaction takes place. It does not tarnish at ordinary temperatures and resembles palladium in that it may be only slightly oxidized at red heat. Exposure to higher temperatures causes the oxide to decompose, leaving a bright surface.

Compounds

Iridium forms several chlorides, all of which are precipitated as the insoluble brown iridic sulfide when hydrogen sulfide is passed through the solution. Ammonium sulfide exerts the same effect upon iridium chloride solutions.

Double salts are formed from the chlorides of iridium and potassium. These compounds are insoluble in an excess of saturated potassium chloride solution. Ammonium chloroiridate is formed when ammonium chloride is added in excess to iridium solutions. Ammonium chloroiridate is the basis for the separation of the metal. It is ignited to spongy iridium or iridium-black. Ammonium chloroiridate forms dark red crystals which are insoluble in a saturated solution of ammonium chloride.

Iridium salts in alkaline solution are reduced by alcohol to insoluble iridous compounds, in acid solution the addition of zinc causes precipitation of metallic iridium. Iridium, along with several other members of the platinum family, forms sesquioxides, e.g., Ir_2O_3. Ruthenium, rhodium, and osmium act similarly.

Iridium-Blacks

Iridium is precipitated as iridium-black when solutions of the sulfate are exposed to ultraviolet light. Iridium-black is extremely active, usually more so than platinum-black. When alcohol is dropped upon iridium-black, it bursts into flame. A stream of coal gas will also catch fire when directed on iridium-black.

Iridium-black may also be precipitated from an acid solution of the chloride by zinc. Fused iridium is insoluble in aqua regia but iridium-black may be dissolved by it. Spongy iridium is soluble in aqua regia to a certain extent, especially when it is prepared by ignition.

When iridium is heated to redness and chlorine is passed over it, the soluble trichloride forms. The solution of iridium chloride may be used for preparing other iridium compounds, iridium-black, or spongy iridium.

Technology

For alloying, iridium is one of the superior platinum metals, since its alloys are usually dense, workable, tough and highly resistant to chemical agents. Much of the present output of iridium goes into the manufacture of special platinum alloys used to tip fountain pens. Osmiridium is also used to tip pens.

Only about 10 per cent of the native osmiridium can be used for pen points, since the grain size may be too small, and it is not practicable to fuse the alloy into larger lumps. Some of the particles cannot be used because their grain structure causes them to break when worked. In manufacturing pen nibs, a suitable-size grain is selected and attached to the end of the pen point with ordinary silver solder. After being mounted, it is cut through to form halves with a diamond saw. At the present time, man-made alloys of iridium, osmium, platinum, and other metals are finding more favor for nibbing fountain pens.

The district which furnishes most of the native alloy for pen points is the Katharinenberg locality in the Ural Mountains

in Russia, about 200 oz often being recovered in a year. Scattered sections of the Urals also contribute to the osmiridium output. The California metal, which contains more iridium and osmium and less platinum, is heavier and much harder than the Russian alloy. The California alloy is preferred because of these properties.

Native osmiridium finds limited application in balance bearings, compasses, and point-bearings for delicate electrical instruments. Osmiridium and other alloys of iridium are well suited for use on hard-wearing surfaces, and this use accounts for much of the demand for iridium, the output usually being far below the demand.

Iridium and many of its compounds possess catalytic properties. Iridium has been used in the catalytic oxidation of ammonia to nitric acid, although the method is not yet extensively used. Iridium chloride will catalyze the reduction of tetravalent platinum to the bivalent state by oxalic acid. Sodium oxychloride is decomposed immediately with iridium chloride into sodium chloride and nascent chlorine.

Today, much of the iridium goes into crucibles and platinum alloys for hardening purposes. The standard meter and standard kilogram contain 10.1 per cent iridium and 89.8 to 89.9 per cent platinum. The balance of this alloy consists of a small amount of osmium, rhodium, palladium, and/or ruthenium. Platinum-iridium alloys, like platinum-rhodium alloys, are also employed for thermocouples and thermoelectric thermometers or pyrometers, which are so largely used for accurate determination of temperatures during the working of metals and alloys.

The addition of small quantities of iridium to platinum not only imparts strength and increases its melting point, but also increases its hardness. Platinum-iridium alloy is therefore less easily worked than pure platinum and must be swaged with zinc counter-dies. Plates of platinum-iridium alloy, like those of pure platinum, can be soldered with pure gold, silver and gold, and silver solders.

Osmium

Physical Properties

Osmium has the highest density of all known matter, i.e., 22.5. Pure osmium is very rare. It is brittle and non-malleable. Osmium is hard enough to scratch glass. The pure metal usually has a tin-white color with a distinct gray-blue tint, but, like the other platinum metals, the color varies with the state of the metal. The melting point of pure osmium is not known with certainty, the best value to date being between 2600 and 2700°C. The same can be stated for the boiling point, which is about 5300°C.

TABLE 42

Physical Properties of Osmium

Property	*Value*
Specific gravity	22.5
Melting point	2700°C
Boiling point	5300°C
Volatility at 1300°C (Os = 1000)	1000
Linear coefficient of expansion at 0°C	5.7×10^{-6}
Moh hardness, cast	7.0

Chemical Properties

Unlike the other platinum metals, osmium burns in air when strongly heated, forming the volatile tetroxide. Chemically speaking, osmium is very complex, having four different valences: two, three, four, and eight. It is one of the few elements having a valence of eight. Osmium is like carbon in its response to heat, since it vaporizes without melting. Its detection and separation from other platinum metals, particularly iridium, are based upon this property.

Compounds

Osmium forms osmates, chlorides, fluorides, five different oxides, and many complex compounds. All osmium compounds, when boiled with an excess of nitric acid, emit the pungent odor of the tetroxide, a compound in which the osmium apparently has a valence of 8.

Osmium tetroxide is often called *osmic acid*, although it does not act as an acid. Osmium tetroxide is one of the most powerful oxidizing agents known. Its oxidizing property is utilized in histologic work and for special chemical reactions. For example, alcohol is immediately converted into the aldehyde in the presence of osmic acid, indigo solution is decolorized, and iodine is separated from potassium iodide. Most compounds of osmium yield metallic osmium when ignited in a current of hydrogen.

Extraction and Preparation

To extract osmium from osmiridium, the most important source of the element, powdered osmiridium is mixed with an equal amount of sodium chloride and heated in a porcelain boat inside a glass tube at dull-red heat, while a current of chlorine is allowed to pass over it. The double chlorides of osmium and iridium are formed in this treatment.

The mass consists of double chlorides. After cooling, it is dissolved in boiling water and the solution is concentrated by evaporation. The liquor is acidified with nitric acid and distilled. The osmium passes over as the tetroxide and is collected by allowing the end of the condenser to dip into potassium hydroxide solution. The resulting solution, containing the osmium, is then evaporated to dryness with an excess of ammonium chloride. The solid product is ignited, washed with water, and dried. The osmium metal remains as a black to gray powder with a slight metallic luster.

In preparing powdered osmiridium for fusion, the alloy is

first fused with zinc and a small amount of ammonium chloride. The zinc is dissolved from the fusion product with dilute sulfuric acid. Osmium and iridium remain as impalpable powders.

The solution of iridium remaining after distillation of the osmium is concentrated by evaporation, and ammonium chloride is added to precipitate the iridium as ammonium chloriridate. Upon ignition of this compound, spongy iridium is obtained.

Analysis

In the test for osmium devised by Singleton,[41] a coloration is produced with as little as 0.1 mg of thiocarbanilide per cubic centimeter. On extraction with ether the sensitivity increases, a deep-red color being formed. Osmates produce a red color with thiourea and a pinkish hue is noted with as little as 0.01 mg of osmium per cc.

Osmium, as osmium tetroxide, may be detected by adding a concentrated solution of potassium thiocyanate to the solution to be tested in hydrochloric, nitric, or sulfuric acid, and extracting with ether or amyl alcohol. A deep-blue color appears in the extraction layer. The test is sensitive to 1 part in 1,000,000.[42]

A very sensitive microchemical test for osmium consists of adding 1 drop of hydrochloric acid to 1 drop of the solution to be tested, followed by a drop of concentrated pyrogallol solution. A blue coloration is formed by as little as 10 gammas of osmium per cc.[43] Palladium gives a green color, as does platinum, while gold produces a violet color.

Osmates may be detected by adding 1 drop of a saturated aqueous solution of ephedrine hydrochloride to the osmate solution. On adding sodium hydroxide an orange color forms. The sensitivity is increased by shaking out with carbon tetrachloride, forming an amber-yellow color.

In testing for osmium, 1 to 2 cc of the solution to be tested are placed in a test tube and a stopper inserted which carries

a short length of narrow tubing ending in a fine opening. A piece of filter paper is moistened with potassium ferrocyanide and another piece with an acetic acid solution of benzidine. On heating the solution and bringing the treated paper near the opening for ½ minute, a violet coloration is produced in the benzidine paper, and a green color forms in the ferrocyanide paper.[44]

Technology

Osmium finds some use in an alloy with iridium for pen points and for the bearings of fine balances. Its compounds find more use than the pure metal, which is both expensive and difficult to work. Osmium tetroxide, or *osmic acid*, is used in histology to stain nerve and medullary tissues. It is believed that the black stain which is produced on organic substances is the hydrated osmium dioxide. The oxide is a very good oxidizing agent.

Osmium tetroxide has been used orally for the treatment of epilepsy. Potassium osmate has been injected subcutaneously for the treatment of neuralgia, cancer, strumous glands, sarcoma, and sciatica. The oral dose is very small, because the compound is extremely poisonous, and its fumes are very irritating to lung tissue. About 10 mg is the maximal dose prescribed. At present, however, it is rarely used. Ten drops of a 2 per cent solution were once employed for injection directly in nerve tissue.

Since osmium tetroxide turns black when it comes in contact with organic matter, it has found use in fingerprinting, and for bringing out latent palm and sole impressions. It is especially adapted to work on paper and wood.

Both osmium tetroxide and osmium metal are powerful catalysts. Osmium tetroxide is finding increasing application in the catalysis of hydroxylations.[45] Osmium tetroxide is known by several names other than osmic acid, e.g., perosmic anhydride. perosmic acid, and hyperosmic acid.

Rhodium

Physical Properties

Pure rhodium metal is useful for plating and for the production of acid-resisting surfaces. Rhodium is a whitish-gray metal resembling aluminum, often having a bluish tinge. The metal is softer than osmium or ruthenium and melts at a lower temperature. Its name is derived from the Greek *rhodon*, meaning rose-red, after the color of its salts. Rhodium is less malleable and ductile than platinum. It belongs to the light group of platinum metals, having a specific gravity of 12.44.

Like palladium and silver, rhodium absorbs oxygen from the air and *sprouts* on cooling. It readily alloys with many metals. The presence of small amounts of platinum, copper, lead, or bismuth reduces its resistance to acids. Rhodium is not excessively brittle at ordinary temperatures, as are some of the other platinum metals. When heated to redness its malleability increases.

TABLE 43

Physical Properties of Rhodium

Property	*Value*
Specific gravity	12.44
Melting point	1966°C
Boiling point	4300°C
Volatility at 1300°C (Os = 1000)	1
Thermal conductivity at 18°C	0.210 cal/g
Electrical resistivity at 0°C	4.51 microhm-cm
Linear coefficient of expansion at 0°C	8.2×10^{-6}
Brinell hardness, cast	390

Chemical Properties

Pure rhodium resists concentrated aqua regia, but the presence of small amounts of foreign metals make this metal liable to attack. When rhodium is alloyed with gold or silver, aqua

regia does not affect it. Rhodium is oxidizable at red heat, but at ordinary temperatures it does not tarnish. The metal, under suitable conditions, combines with chlorine and other elements to form salts. Pure rhodium withstands boiling with a mixture of aqua regia and concentrated sulfuric acid.

Compounds

Rhodium exhibits three valences, two, three, and four. In its principal compounds it has a valence of two or four. Like many of the metals of the platinum family, rhodium forms numerous compounds of a very complex nature.

The addition of ammonium sulfide or hydrogen sulfide to solutions of rhodium precipitates brown rhodic sulfide, Rh_2S_3. This substance is insoluble in its boiling mother liquor, but dissolves in hot nitric acid solution. Alkali metal hydroxides form hydroxides with rhodium in the presence of alcohol.

Rhodium forms the iodide when potassium iodide solution is added to it. Metallic rhodium is thrown from its solution when metallic zinc is added. The metal thus prepared is in a finely divided state and is known as rhodium-black. Rhodium-black possesses the properties characteristic of other finely divided platinum metals, in that it absorbs oxygen, and therefore acts as a catalyst. Rhodium-black will cause certain organic substances to burst into flame when it comes in contact with them.

Analysis

In order to obtain solution of metallic rhodium, metathesis with potassium bisulfate is usually employed. Solutions of rhodium form double salts with ammonium salts and some alkali metal compounds. Thus, ammonium chlororhodate is formed on careful evaporation of rhodic chloride with ammonium chloride.

One method for the quantitative estimation of rhodium depends on the formation of sodium chlororhodate. The ore is

dissolved in aqua regia, in order to remove the platinum and iridium, and ammonium chloride is added together with alcohol and mercuric cyanide. Palladium precipitates out, the rhodium remaining in solution. The filtrate is saturated with sodium carbonate, hydrochloric acid is added to decompose the excess cyanide, and the liquid is evaporated to dryness. After treating the residue with alcohol, only red-brown sodium chlororhodate will remain, because the remainder of the mass dissolves. Ignition of the sodium chlororhodate in hydrogen yields rhodium.

Titanium sesquisulfate may be employed for detecting iridium and osmium.[46] The reagent is a 1.5 to 2N solution of the titanium salt in 2N sulfuric acid. Rhodium salts reduce this reagent, but iridium salts remain in solution. The titanium sesquisulfate is prepared by the reduction of titanic sulfate with zinc amalgam.

When rhodium salts are heated with stannous chloride, they form brown and then raspberry-red colorations.[47] A yellow precipitate is formed on adding a slight excess of sodium oxychloride to a neutral or slightly acid solution of rhodium ammonium chloride. The precipitate dissolves with an orange-yellow coloration when 1:5 acetic acid is added dropwise. The color soon fades, then a gray precipitate forms, and finally a sky-blue color appears. On adding potassium carbonate a green precipitate is formed.[48]

Technology

Engineers find that rhodium plating adds years of life to an object which must stand much usage and yet retain its beauty and luster. Surgical instruments, for example, are being plated with rhodium, and automobile headlight reflectors have for some time been coated with this bright metal. Rhodium alloys are used in hypodermic needles. Numerous small devices used in specialized fields are plated with or made from rhodium alloy.

Rhodium Alloys

Platinum-rhodium gauze is a very important catalyst. It is used for the oxidation of ammonia to nitric acid. Because of its long life, it has proved superior to pure platinum or palladium. As a result of research in this country and abroad, a rhodium-platinum alloy has been developed for the catalysis of ammonia oxidation, which is now recognized as standard equipment in most nitric acid works of the world.

Rhodium Plating

At present rhodium is the only platinum metal which is being electroplated on an extensive commercial scale.[19] Although rhodium plating was known in academic circles before 1915, it was not until 1930 that extensive use of this metal was made for plating purposes.

In general, only acid electrolytes give a bright, whitish deposit and at the same time have good throwing power. Practically all the successful rhodium-plating solutions are of the acid type. Since rhodium forms a number of complex phosphates whose composition is not known, it is only by rigorous control during rhodium salt manufacture that a uniform product can be obtained. Rhodium-plating preparations are now sold in the form of concentrated solutions.

In rhodium plating, either an acid sulfate solution, or an acid phosphate solution is employed which usually has a metal concentration of 2 g/l. Although this concentration is arbitrary, it has been found through practice to correspond to optimum conditions of drag-out losses and quick coverage. The sulfuric (or phosphoric) acid concentration is not critical; it ranges from 10 cc/l to slightly higher. Higher concentrations of acid tend to lower the cathode efficiency.

A rhodium plating solution of the acid sulfate type is:

Sulfuric acid	20 cc/l
Rhodium metal in prepared concentrated solution	2 g/l

A rhodium plating solution of the acid phosphate type is:

Ortho-phosphoric acid	40 cc/l
Rhodium metal in prepared concentrated solution	2 g/l

In making up the bath it is important to add the acid to the water before adding the rhodium solution. If this is not done, the rhodium may be precipitated by hydrolysis. The best working temperature is between 40 and 45°C. The current density is from 1 to 11 amp per square decimeter. Insoluble platinum anodes are used. The metal content is replenished by the addition of more rhodium solution.

With such a solution a bright deposit of rhodium appears in 30 minutes. It is about 0.00015 cm thick and does not require buffing. Usually a nickel undercoating is used for rhodium plating on all surfaces except gold alloy and platinum surfaces. Zinc, tin, and lead alloys must have a heavy coating of nickel to protect the base metal from the action of the rhodium solution.

Rhodium deposits have a high reflectivity and a hardness between that of nickel and chromium. Good results are obtained in flash plating, but for silverware and high grade reflectors greater thickness is preferable.

Fink and Lambros [50] have also devised a method for rhodium plating. Several patents have been granted to Baker and Company for similar procedures.[51]

Ruthenium

Physical Properties

Pure ruthenium is a very scarce metal. It is gray in color when impure or powdered but resembles platinum in color when massive. Like the other metals, ruthenium in the finely divided state is less resistant to acids, a factor of importance in its working and extraction. The specific gravity of ruthenium

is 12.2; it is the denser member of the light group of platinum metals. Ruthenium is both hard and brittle; it is probably much harder than any other platinum metal, having a Brinell hardness, when annealed, of about 220, as against 172 for iridium.

Finely divided ruthenium may be used as a catalyst. Ruthenium is hardened by mechanical treatment but may be softened by annealing or heating to a suitable temperature. The metal is almost as difficult to fuse as osmium; its melting point is about 2450°C.

TABLE 44

PHYSICAL PROPERTIES OF RUTHENIUM

Property	*Value*
Specific gravity	12.2
Melting point	2450°C
Boiling point	4500°C
Volatility at 1300°C (Os = 1000)	200
Electrical resistivity at 0°C	14 microhm-cm
Brinell hardness, annealed (120 kg load)	220

Chemical Properties

Ruthenium oxidizes slowly in air. Oxidation is accelerated at higher temperatures, giving rise to a bluish-black coating of ruthenic oxide. When ruthenium is heated in an atmosphere of oxygen, it burns with a smoky flame, producing brilliant sparks and generating ozone. Ruthenium is attacked by halogens, especially chlorine, but acids and aqua regia do not affect it appreciably.

Compounds

Ruthenium has six valences: two, three, four, six, seven, and eight. Ruthenium in the higher valence states acts much like hexavalent and heptavalent manganese, forming ruthenates, such as K_2RuO_4, and perruthenates, such as $KRuO_4$. The

element forms a tetroxide, RuO_4, which does not have strong acidic or basic properties. Ruthenium dioxide is amphoteric and in its lower valence states forms metallic salts. The tetroxide is produced by allowing chlorine gas to pass through a hot, alkaline solution of a ruthenium salt in distillation apparatus. Like osmium tetroxide, the ruthenium tetroxide is volatile. Ruthenium tetroxide forms golden-yellow crystals which melt at 85°C. It decomposes explosively at 108°C in the presence of a trace of organic matter.

Very small amounts of ruthenium in solution precipitate as the brownish-blue sulfide on the addition of hydrogen sulfide. The test, however, must be conducted with care, since the solution turns a delicate blue before the sulfide forms. Ammonium sulfide forms a brownish-black precipitate. Alkali metal hydroxides, such as sodium hydroxide, form black ruthenic hydroxide, $Ru_2(OH)_6$, which is insoluble in an excess of mother liquor but decomposes in acids.

Preparation of Metallic Ruthenium

Metallic ruthenium may be obtained from its solutions by the addition of metallic zinc, producing at first a fine azure-blue color because of the reduction of the salts, and finally depositing as blackish metallic ruthenium. Ruthenium forms double salts, exemplified by the addition of potassium or ammonium chloride to concentrated ruthenium, from which crystalline precipitates of violet-colored double chlorides form.

Metallic ruthenium is obtained in large-scale operations from the treatment of platinum ore residues remaining after the aqua regia extraction. The residue is finely powdered by zinc fusion, as described under osmium. The resulting powder is heated with a mixture of 3 parts barium oxide and 1 part barium nitrate to about 950°C. The cooled fusion product is immediately transferred to a stoppered vessel to prevent loss of osmium by volatization of the tetroxide.

After all action has ceased, 1 part nitric acid and 2 parts sulfuric acid are added and the mixture shaken, allowed to settle,

and the solution obtained decanted from the precipitate of barium sulfate which forms. The liquid is then distilled to remove the osmium. The equally volatile ruthenium tetroxide is not produced under these conditions.

The residue is mixed with 3 parts ammonium chloride and a small quantity of nitric acid, evaporated, and washed with a mixture of 1 part saturated ammonium chloride solution and 1 part water. The washing is continued until the filtrate is colorless. The residue contains ammonium chloroiridate and ammonium chlororuthenate, and is then ignited. The metals are then fused for several hours in a silver crucible with a mixture of 2 parts potassium nitrate and 1 part potassium carbonate. The fusion product is dissolved in water; the bluish potassium iridate remains as an insoluble product.

The solution containing ruthenium is treated with nitric acid until the yellowish-red color due to potassium ruthenate disappears, and the ruthenium precipitates as the oxide. The oxide is filtered off, reduced in a graphite crucible, and fused with an oxyhydrogen flame or in an electric furnace.

Analysis

When ruthenium salts are boiled with phloroglucinol in an alkaline solution of potassium nitrite, a dark-violet color forms. On heating ruthenium salts with allyl thiourea a blue solution is obtained,[52] and with *p*-nitrosophenol a dark violet solution is obtained. Platinum salts give a blood-red solution with pyrocatechol or pyrogallol, and an ammonical platinum solution gives the same color with resorcinol. Iridium salts form a deep-blue color when heated with aniline sulfate. Osmium salts produce a dark-rose color when heated with aniline sulfate, although the osmium must be in the form of potassium osmate. Potassium chlorosmite forms a violet color with aniline sulfate and a blue color with β-naphthylamine, pyrocatechol, or pyrogallol.

Ruthenium salts and osmium may be detected by the methods of Wohler and Metz.[53] When ruthenium solutions are heated

a short time with thiourea and hydrochloric acid, a blue color forms. The test is sensitive to 3 gammas per cc. On substituting thiocarbanilide a blue-green color forms and this can be shaken out with ether, making the reaction 10 times as delicate.

In testing for ruthenium in solids, especially in ore residue, chlorine is passed over a warm mixture of residue containing 1 cc of hydrochloric acid to oxidize the ruthenium to ruthenium tetroxide, which dissolves in the acid, forming a blue solution. The test is claimed to be sensitive to 1 gamma.[54] A similar reaction is based on the conversion of ruthenium to ruthenium tetroxide, the vapors of which blacken paper.[55]

Technology

Ruthenium has not found very many applications in either the laboratory or in industry. The reasons for this are numerous. Ruthenium is an expensive metal and therefore its metallurgy has not been fully developed. Its chemistry is not well known. A few medicinals have been developed containing ruthenium. A compound used for treating syphilis at one time had ruthenium in its structure.

Ruthenium Red

A dye known as ruthenium red has been developed, which is chemically ruthenium tetramminohydroxychlorochloride. It stains silk a fast red color. It is employed in aqueous solution. It may also be used to color wool a dull rose, which is not permanent. Cotton and some of the other fibers are not affected by ruthenium red. Its use is not widespread because of the cost of ruthenium and the stiff competition provided by organic dyes.

Ruthenium salts find limited use in histologic work for staining tissues. The ruthenium red is used in aqueous solution for staining pectin, gum, bacteria, and animal tissues. It is a brownish-red powder containing 36.81 per cent ruthenium. It

is also known by the name of ammoniated ruthenium oxychloride.

Ruthenium salts tend to hydrolyze on slight heating. Therefore, their application in medicine has met with some discouragement. However, when a nitroso group is introduced into the compound a very stable salt results. It is this approach which may make the application of ruthenium to medicine possible. It has been used with some success in the treatment of tuberculosis.

Ruthenium Plating and Alloys

A ruthenium alloy that may be of importance for jewelry consists of palladium hardened by ruthenium and rhodium. A typical formula is 95 parts palladium, 2 to 4 parts ruthenium, and the remainder rhodium. This alloy has a low specific gravity. The working quality is good. The color is identical with that of platinum and it is non-tarnishable.

Comparatively little work has been done on ruthenium plating, although one patent does exist on the subject.[58] An acid-ruthenium bath is employed:

Sulfuric acid	20 cc/l
Ruthenium nitrosochloride	4 g/l

A dark deposit is obtained from this preparation. A current density of 2.2 amperes per square decimeter at a voltage of 2.5 V is used. Ruthenium plating may be important for special purposes which require physical properties characteristic of this metal in the pure state.

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APPENDICES

APPENDIX I

Abridged Bibliography of Rarer Elements

By R. B. Gordon

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APPENDIX II

INTERNATIONAL TABLE OF ATOMIC WEIGHTS—1941 *

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.010
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.357
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium	Cb	41	92.91
Copper	Cu	29	63.57
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.76
Iodine	I	53	126.92
Iridium	Ir	77	193.1

* J. Am. Chem. Soc. **63** [3] (1941).

Iron	Fe	26	55.85
Krypton	Kr	36	83.7
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutecium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	20	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16.0000
Palladium	Pd	46	106.7
Phosphorus	P	15	30.98
Platinum	Pt	78	195.23
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protoactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rd	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.06
Tantalum	Ta	73	180.88
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12

Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

APPENDIX III

PERIODIC SYSTEM OF THE ELEMENTS *

O	I	II	III	IV	V	VI	VII	VIII
R	RH R_2O	RH_2 RO	RH_3 R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	 RO_4
He 2 4.002	**Li** 3 6.940	**Be** 4 9.02	**B** 5 10.82	**C** 6 12.00	**N** 7 14.008	**O** 8 16.0000	**F** 9 19.00	
Ne 10 20.183	**Na** 11 22.997	**Mg** 12 24.32	**Al** 13 26.97	**Si** 14 28.06	**P** 15 31.02	**S** 16 32.06	**Cl** 17 35.457	
A 18 39.944	**K** 19 39.10	**Ca** 20 40.08	**Sc** 21 45.10	**Ti** 22 47.90	**V** 23 50.95	**Cr** 24 52.01	**Mn** 25 54.93	**Fe** 26 55.84 **Co** 27 58.94 **Ni** 28 58.69
	Cu 29 63.57	**Zn** 30 65.38	**Ga** 31 69.72	**Ge** 32 72.60	**As** 33 74.93	**Se** 34 79.2	**Br** 35 79.916	
Kr 36 83.7	**Rb** 37 85.44	**Sr** 38 87.63	**Y** 39 88.92	**Zr** 40 91.22	**Cb** 41 93.3	**Mo** 42 96.0	**Ma** 43	**Ru** 44 101.7 **Rh** 45 102.91 **Pd** 46 106.7
	Ag 47 107.880	**Cd** 48 112.41	**In** 49 114.8	**Sn** 50 118.70	**Sb** 51 121.76	**Te** 52 127.5	**I** 53 126.92	
Xe 54 131.3	**Cs** 55 132.81	**Ba** 56 137.36	* 57–71	**Hf** 72 178.6	**Ta** 73 181.4	**W** 74 184 0	**Re** 75 186.31	**Os** 76 190.8 **Ir** 77 193.1 **Pt** 78 195.23
	Au 79 197.2	**Hg** 80 200.61	**Tl** 81 204.39	**Pb** 82 207.22	**Bi** 83 209.00	**Po** 84	85	
Rn 86 222	87	**Ra** 88 225.97	**Ac** 89	**Th** 90 232.12	91	**U** 92 238.14		

*Rare Earths:

La 57	**Ce** 58	**Pr** 59	**Nd** 60	Il 61	**Sm** 62	**Eu** 63	**Gd** 64	**Tb** 65	**Dy** 66	**Ho** 67	**Er** 68	**Tm** 69	**Yb** 70	**Lu** 71
138.92	140.13	140.92	144.27	—	150.43	152.0	157.3	159.2	162.46	163.5	167.64	169.4	173.5	175.0

* J. Am. Chem. Soc., **59**, 269 (1937).

The following elements have not been adopted by the Committee on Atomic Weights. They can, however, be given a place in the Periodic System of the Elements.

Element	*Symbol*	*Atomic Number*	*Atomic Weight*
Actinium	Ac	89	229
Alabamine	Ab	85	> 126
Illinium	Il	61	146(?)
Masurium	Ma	43	> 54
Polonium	Po	84	218
Virginium	Vi	87	> 132
Neutron	$_0n^1$	0	1^+

APPENDIX IV

AVERAGE PER CENT OF SPECIFIED METALS IN IGNEOUS ROCKS

Rank	*Metal*	*Per Cent*
	Over 0.01 per cent	
1	Silicon	27.72
2	Aluminum	8.13
3	Iron	5.01
4	Calcium	3.63
5	Sodium	2.85
6	Potassium	2.60
7	Magnesium	2.09
8	Titanium	0.63
9	Manganese	0.10
10	Barium	0.050
11	Chromium	0.037
12	Zirconium	0.026
13	Nickel	0.020

*Clarke and Washington, "The Composition of the Earth's Crust," *U. S. Geol Survey, Professional Paper*, **127**, Washington, 1924.

Under 0.01 but over 0.001 per cent

14	Strontium	1.9×10^{-4}
15	Vanadium	1.7×10^{-4}
16	Rare earths	1.5×10^{-4}
17	Copper	1.0×10^{-4}
18	Uranium	8×10^{-5}
19	Tungsten	5×10^{-5}
20	Lithium	4×10^{-5}
21	Zinc	4×10^{-5}
22	Columbium and Tantalum	3×10^{-5}
23	Hafnium	3×10^{-5}
24	Thorium	2×10^{-5}
25	Lead	2×10^{-5}
26	Cobalt	1×10^{-5}
27	Beryllium	1×10^{-5}

Under 0.001 per cent

28		
29	Rubidium	$n \times 10^{-6}$
30	Arsenic	$n \times 10^{-6}$
31	Tin	$n \times 10^{-6}$
32	Cesium	$n \times 10^{-7}$
33	Scandium	$n \times 10^{-7}$
34	Antimony	$n \times 10^{-7}$
35	Cadmium	$n \times 10^{-7}$
36	Mercury	$n \times 10^{-7}$
37	Bismuth	$n \times 10^{-8}$
38	Silver	$n \times 10^{-8}$
39	Selenium	$n \times 10^{-8}$
40	Platinum	$n \times 10^{-9}$
41	Tellurium	$n \times 10^{-9}$
42	Gold	$n \times 10^{-9}$
43	Iridium	$n \times 10^{-10}$
44	Osmium	$n \times 10^{-10}$
45	Thallium	$n \times 10^{-10}$
46	Indium	$n \times 10^{-11}$
47	Gallium	$n \times 10^{-11}$
48	Rhodium	$n \times 10^{-11}$
49	Palladium	$n \times 10^{-11}$
50	Ruthenium	$n \times 10^{-11}$
51	Germanium	$n \times 10^{-11}$
52	Radium	$n \times 10^{-12}$

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