CESIUM AND CESIUM COMPOUNDS

1. Introduction

Cesium [7440-46-2], Cs, is a member of the Group 1 (IA) alkali metals. It resembles potassium and rubidium in the metallic state, and the chemistry of cesium is more like that of these two elements than like that of the lighter alkali metals.

Cesium, first discovered by Bunsen and Kirchoff in 1860 while examining spring water, was the first element discovered spectroscopically (1). The name, comes from the Latin *caesius,* sky blue, and refers to the characteristic blue spectral lines of the element. Cesium salts were not successfully reduced to metal until 1881. Electrolysis of the molten chloride did not yield cesium metal under the same conditions that led to the reduction of the other alkali metal chlorides.

Cesium was first produced in the metallic state by electrolysis of a molten mixture of cesium and barium cyanides (2). Subsequently the more common thermochemical–reduction techniques were developed (3,4). There were essentially no industrial uses for cesium until 1926, when it was used for a few years as a getter and as an effective agent in reducing the electron work function on coated tungsten filaments in radio tubes. Development of photoelectric cells a few years later resulted in a small but steady consumption of cesium and other applications for cesium in photosensing elements followed.

Until the late 1970s, cesium continued to be little more than a research element. Much of its limited production was for research into thermionic power conversion, magnetohydrodynamics (qv), and ion propulsion. Although the potential for these applications has not materialized, cesium chemical usage has increased significantly as catalysts in the chemical and petrochemical industries and in biotechnical engineering (see GENETIC ENGINEERING; NUCLEIC ACIDS).

2. Physical Properties

Pure cesium is a silvery white, soft, ductile metal. Surface alteration by minute traces of oxygen result in the metal taking on a golden hue. Of the stable alkali metals, ie, excluding francium, cesium has the lowest boiling and melting point,

Table 1. **Physical Properties of Cesium**

Property	Value
atomic number	55
atomic weight	132.905
melting point, °C	29
boiling point, °C	685
specific gravity, kg/m^3	
solid at 17°C	1892
liquid at 40°C	1827
atomic radius,[a] nm	0.274
ionic radius,[b] nm	0.165
viscosity at mp, mPa · s (=cP)	0.686
surface tension at mp, mN/m	39.4
heat of fusion, ΔH_{fus}, kJ/mol[c]	2.13
heat of vaporization, ΔH_{vap}, at 0.1 MPa, J/mol[c,d]	65.9
specific heat, J/g · °C[c]	
solid at 20°C	0.217
liquid at bp	0.239
vapor at bp	0.156
thermal conductivity, W/(m · °C)	
liquid at mp	18.4
vapor at bp	4.6×10^{-3}
ionization potential, eV	3.893
work function, eV	1.91
standard electrode potential, V	−2.923
electrical conductivity, $(\Omega \cdot \text{m})^{-1}$	
solid at mp	4.9×10^{6}
vapor at 1250°C	2.0×10^{4}
Moh's hardness	0.2
Brinell hardness, kg/mm^2	0.015

[a] The metal is 12 coordinate.

[b] The ion is usually six coordinate.

[c] To convert J to cal, divide by 4.184.

[d] To convert MPa to psi, multiply by 145.

the highest vapor pressure, the highest density, and the lowest ionization potential. These properties and the large radius of the monovalent cesium ion have important consequences directly related to applications (5). Selected physical properties are given in Table 1.

3. Chemical Properties

The ionization potential of the alkali metals decreases with increasing atomic number; consequently cesium is generally far more reactive than the lower members of the alkali metal group. When cesium is exposed to air, the metal ignites spontaneously and burns vigorously producing a reddish violet flame to form a mixture of cesium oxides. Similarly cesium reacts vigorously with water to form cesium hydroxide, the strongest base known, as well as hydrogen; together with air and water a hydrogen explosion usually occurs as the burning cesium readily ignites the liberated hydrogen gas. Cesium, the most active of the alkali metals toward oxygen and the halogens, is the least reactive toward nitrogen, carbon, and hydrogen.

Cesium salts are, in general, chemically similar to other alkali metal salts. The solubility of alkali metal salts of simple anions generally increases with the atomic weight of the alkali ion; in contrast the solubility of the alkali metal salts of complex anions generally decreases with increasing atomic weight. The salts of cesium and simple anions are usually hygroscopic as well as very soluble, but the sparingly soluble salts of cesium and complex anions are seldom hydrated and are usually not hygroscopic.

Cesium forms simple alkyl and aryl compounds that are similar to those of the other alkali metals (6). They are colorless, solid, amorphous, nonvolatile, and insoluble, except by decomposition, in most solvents except diethylzinc. As a result of exceptional reactivity, cesium aryls should be effective in alkylations wherever other alkaline alkyls or Grignard reagents have failed (see GRIGNARD REACTIONS). Cesium reacts with hydrocarbons in which the activity of a C–H link is increased by attachment to the carbon atom of doubly linked or aromatic radicals. A brown, solid addition product is formed when cesium reacts with ethylene, and a very reactive dark red powder, triphenylmethylcesium [76-83-5], $(C_6H_5)_3CCs$, is formed by the reaction of cesium amalgam and a solution of triphenylmethyl chloride in anhydrous ether.

4. Occurrence

Cesium is the rarest of the naturally occurring alkali metals, ranking fortieth in elemental prevalence. Nevertheless, it is widely distributed in the earth's crust at very low concentrations. Granites contain an average of $\sim$1 ppm (7), sedimentary rocks $\sim$4 ppm (8), and seawater $\sim$0.2 ppm (9). Higher concentrations are found in lepidolite [1317-64-2], a lithium mica containing $\sim$0.5% Cs_2O but reaching 1.9% on rare occasions (10), in carnallite [1318-27-0], $KMgCl_3{\cdot}6H_2O$, a double salt of potassium and magnesium chlorides containing 10–40 ppm Cs_2O; in the rare mixed-cesium–antimony–tantalum oxide cestibtantite (11); as well as in muscovite, beryl, spodumene, potassium feldspars, leucite, petalite, and related minerals. Both lepidolite and carnallite have yielded commercial quantities of cesium (12) and a process for its recovery from muscovite micas has been developed (13).

By far, the most important commercial cesium source is pollucite [1308-53-8], ideally $Cs_2O{\cdot}Al_2O_3{\cdot}4SiO_2$. The theoretical cesium content of pure pollucite is 45 wt% Cs_2O; however, natural pollucite usually contains 5–32% Cs_2O because of other minerals intimately associated with the pollucite. Additionally, the Cs is often replaced in the crystal lattice by varying amounts of Rb, K, or Na plus H_2O. Natural pollucite can be regarded as an intermediate mineral in the isomorphous series analcime [1318-10-1], $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$, and theoretical pollucite (14). Pollucite is a clear to milky greyish mineral with uneven fracture, similar to quartz but from which it can generally be distinguished by the ubiquitous veinlets of alteration products that occur in the pollucite (14). Alternatively, a qualitative field test that produces a bright red reaction stain (15) can be used to ascertain its presence.

Table 2. **World Mine Production, Reserves, and Reserve Base of Cesium**[a]

Country	Reserves[b], kg	Reserve base[b], kg
Canada	70,000,000	73,000,000
Namibia		9,000,000
Zimbabwe	23,000,000	23,000,000
other countries	na	na
World total (rounded)	*100,000,000*	*110,000,000*

[a] From Ref. 18, estimated, based on the occurrences of pollucite.
[b] na = not available.

Economic concentrations of pollucite usually occur in highly zoned complex pegmatites, associated with lepidolite, petalite, and spodumene. The Bernic Lake orebody of Tantalum Mining Corp. of Canada Ltd. (Tanco) in southeastern Manitoba, Canada, is the world's largest cesium source containing approximately two-thirds of the known ore. The pollucite occurs as essentially monomineralic zones within a flat lying pegmatite having a spatial extent of some 3 km^2. The main zones contain over 400,000 tons of pollucite grading ~24% Cs_2O with another zone of 100,000 tons of 5% ore (16). Tanco's production accounts for about two-thirds of the world's requirements. Other significant ore deposits are the Bikita pegmatite in Zimbabwe, and in the Karibib desert of Namibia (17). Other, smaller concentrations occur in China and Brazil, where some production takes place, as well as Scandinavia, Czechoslovakia, Afghanistan, and the United States. Some ore was mined from a deposit in Maine between World Wars I and II, but there has been no U.S. production for several decades. Russia has some low-grade resources, but the evidence points to them not being exploited, presumably because of low grade. The known high grade reserves of pollucite are sufficient to supply a steady demand for well over a century, and since 1960, cesium has essentially been produced from pollucite.

The estimates of reserves and reverse base are based upon occurrences of pollucite and are shown in Table 2 (18).

5. Processing of Pollucite

Pollucite preparation consists simply of mining the ore, crushing it to required size, followed in some instances by hand picking. No other concentration is required. Although flotation processes for the concentration of low grade ores have been developed in both the United States and Russia (19), these have commercially lagged because of the availability of high grade ores (20). Chemtall 6 mbh is the predominant processor worldwide. The only significant U.S. producer is Fluids (Woodland, Texas). Their production plant is in Bernic Lake, Manitoba, Canada. Canada is the major source of cesium ores. Other sources are found in United Kingdom (18)

There are three basic methods of converting pollucite to cesium metal or compounds: direct reduction with metals; decomposition with bases; and acid digestion. In each case, grinding of the ore to 75 μm precedes conversion.

5.1. Direct Reduction with Metals. Pollucite can be directly reduced by heating the ore in the presence of calcium to 950°C in a vacuum (21), or in the presence of either sodium or potassium to 750°C in an inert atmosphere (22). Extraction is not complete. Excessive amounts of the reducing metal is required and the resultant cesium metal is impure except when extensive distillation purification is carried out. Engineering difficulties in this process are significant, hence, this method is not commercially used.

5.2. Decomposition with Bases. Alkaline decomposition of pollucite can be carried out by roasting pollucite with either a calcium carbonate–calcium chloride mix at 800–900°C or a sodium carbonate–sodium chloride mix at 600–800°C followed by a water leach of the roasted mass, to give an impure cesium chloride solution that is separated from the gangue by filtration (23). The solution can then be converted to cesium alum [7784-17-0], $Cs_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$. Extraction of cesium from the pollucite is almost complete. Solvent extraction of cesium carbonate from the cesium chloride solution using a phenol in kerosene has also been developed (24).

5.3. Acid Digestion. Acid digestion of pollucite is the primary commercial process for cesium production. Hydrofluoric, hydrobromic, hydrochloric, and sulfuric acids can be used. Hydrofluoric acid has been used in Germany (25); it gives the most complete cesium recovery, but the inherent difficulties with its use eliminate any current advantage. Likewise, the proposed hydrobromic acid process (26), which converts pollucite to the bromide that is precipitated using isopropyl alcohol from which the cesium is removed by liquid bromine, is not in use in part because of the engineering problems associated with the hot acids.

Hydrochloric acid digestion takes place at elevated temperatures and produces a solution of the mixed chlorides of cesium, aluminum, and other alkali metals separated from the siliceous residue by filtration. The impure cesium chloride can be purified as cesium chloride double salts such as cesium antimony chloride [14590-08-0], $4CsCl{\cdot}SbCl_3$, cesium iodine chloride [15605-42-2], Cs_2Cl_2I, or cesium hexachlorocerate [19153-44-7], $Cs_2[CeCl_6]$ (27). Such salts are recrystallized and the purified double salts decomposed to cesium chloride by hydrolysis, or precipitated with hydrogen sulfide. Alternatively, solvent extraction of cesium chloride direct from the hydrochloric acid leach liquor can be used.

Sulfuric acid digestion has been investigated by several laboratories, including the Canadian Mines Branch (CANMET), Ottawa, Canada (28). Pollucite is digested at 110°C, close to the boiling point of 35–40% sulfuric acid, followed by a hot water wash and filtration. Cesium alum is crystallized from the leach filtrate by stage cooling to 50°C and then to 20°C, and roasted in the presence of 4% carbon

$$\begin{aligned} Cs_2SO_4 \cdot Al_2(SO_4) \cdot 4H_2O + 1.5\ O_2 + 3\ C \longrightarrow\ & 24\ H_2O + Cs_2SO_4 \\ & + 3\ SO_2 + 3\ CO_2 + Al_2O_3 \end{aligned}$$

The residue is leached to give cesium sulfate solution, which can be converted to cesium chloride by ion exchange on Dowex 50 resin and elution with 10% HCl, treatment using ammonia or lime, to precipitate the aluminum, or by solvent extraction, followed by purification at neutral pH using hydrogen peroxide or ammonia.

In one process developed by Carus Corp., Illinois, pollucite is digested with sulfuric acid to cesium alum that is dissolved in an aqueous hydroxide solution to form cesium alum hydroxide and potassium sulfate, from which cesium permanganate is directly precipitated by addition of potassium permanganate (29).

$$CsAl(SO_4)_2 \cdot 2\,H_2O + 4\,KOH \longrightarrow CsAl(OH)_4 + 2\,K_2SO_4 + 12\,H_2O$$

$$CsAl(OH)_4 + KMnO_4 \longrightarrow CsMnO_4(s) + KAl(OH)_4$$

Alternatively, permanganate can be added to the cesium chloride resulting from hydrochloric acid digestion, after removal of excess iron and alumina by precipitation as hydroxides, followed by centrifugation and filtration (30) to pure cesium permanganate. The resultant cesium permanganate can be converted to the carbonate or chloride by reduction using an agent such as methanol.

6. Production of Cesium Metal

6.1. Thermochemical Methods. Cesium halides can readily be reduced using calcium or barium, but not magnesium. Purified cesium chloride and calcium in roughly equal proportions are heated together to 700–800°C under a vacuum or in an atmosphere of an inert gas such as argon or helium, and 90–95% of the cesium is distilled as metal (31), although lower temperatures (300–400°C) and higher vacuum achieve the same result but with higher purity (32).

$$2\,CsCl + Ca \longrightarrow CaCl_2 + 2\,Cs$$

Magnesium is used to obtain cesium metal from cesium hydroxide [21351-79-1], Cs(OH), cesium carbonate [534-17-8], Cs_2CO_3, or cesium aluminate [20281-00-9], $Cs_2O \cdot Al_2O_3$, according to the following equations (32):

$$2\,CsOH + 2\,Mg \longrightarrow 2\,MgO + H_2 + 2\,Cs$$

$$Cs_2CO_3 + 3\,Mg \longrightarrow 3\,MgO + C + 2\,Cs$$

$$CsO \cdot Al_2O_3 + Mg \longrightarrow MgO \cdot Al_2O_3 + 2\,Cs$$

Vacuum redistillation at low temperature is used for final purification of the cesium metal, if required.

6.2. Thermal Decomposition. Cesium azide [22750-57-8], CsN_3, which is prepared by reacting aqueous solutions of cesium sulfate and barium azide, melts at 326°C and decomposes at 390°C to cesium metal (33):

$$2\,CsN_3 \longrightarrow 3\,N_2 + 2\,Cs$$

6.3. Electrolytic Reduction. The extreme reactivity and relatively high volatility of cesium metal combine to make conventional fused-salt electrolysis of cesium salts impractical for the direct production of cesium metal, although it can be used as one stage in metal production. For example, electrolysis of fused cesium chloride using a molten lead cathode at 700°C results in a cesium–lead alloy containing ~8.5% Cs, from which cesium metal can be distilled at 600–700°C under vacuum (28). Alternatively, electrolysis of concentrated aqueous solutions using a mercury cathode can be followed by distillation of the amalgam resulting in cesium metal (34).

7. Cesium Alloys

Eutectics melting at about −30, −47, and −40°C are formed in the binary systems, cesium–sodium at about 9% sodium, cesium–potassium at ~25% potassium, and cesium–rubidium at about 14% rubidium (35). A ternary eutectic with a melting point of about −72°C has the composition 73% cesium, 24% potassium, and 3% sodium. Cesium and lithium are essentially completely immiscible in all proportions.

Cesium does not alloy with or attack cobalt, iron, molybdenum, nickel, platinum, tantalum, or tungsten at temperatures up to 650°C (36).

8. Cesium Compounds

Cesium compounds are manufactured and distributed by a comparatively large number of companies, considering the size of the total cesium market. Those companies that process pollucite produce their own range of products, some of which are then reprocessed and refined by other, smaller, specialty companies, many of which are located in the United States.

8.1. Carbonates.

Cesium carbonate [534-17-8], Cs_2CO_3, mol wt 325.82, specific gravity 4072 kg/m^3, has theoretical cesium content of 81.58%. It is a colorless, very hygroscopic, crystalline solid, which is stable up to its melting point of 610°C at which temperature it decomposes. The carbonate is prepared from the hydroxide by the addition of carbon dioxide, but it can also be prepared by decomposing the nitrate with excess oxalic acid to form the oxalate and igniting and decomposing the cesium oxalate to the carbonate.

Cesium hydrogen carbonate [15519-28-5], $CsHCO_3$, mol wt 193.92, theoretical cesium content 68.54%, is a colorless, slightly hygroscopic, crystalline solid having a specific gravity of ~1400 kg/m^3, which decomposes at 175°C. It has a solubility of 2.1 kg/L.

8.2. Cesium Chromate.

Cesium chromate [13454-78-9], Cs_2CrO_4, has a mol wt 381.80, and a theoretical cesium content of 69.62 wt%.

8.3. Cesium Halides.

Cesium bromide, [7787-69-1], CsBr, mol wt 212.82, theoretical cesium content 62.45%, is a colorless crystalline solid, having a melting point of 636°C, a specific gravity of 4433 kg/m^3, and a solubility of 1.23 kg/L of water at 25°C. It is usually prepared by neutralizing the carbonate or hydroxide with HBr, but it is also the primary product of the Dow process (26) for pollucite processing.

Cesium chloride, [7647-17-8], CsCl, mol wt 168.36, theoretical cesium content 78.9%, has a melting point of 646°C, a boiling point 1290°C, and a specific gravity of 3983 kg/m^3. Cesium chloride is a primary product of pollucite processing using hydrochloric acid digestion, and it is usually purified by precipitation as a complex double salt, which is then decomposed by hydrolysis or sulfide precipitation, leaving purified cesium chloride in solution. It crystallizes readily from water in well-defined, colorless, cubic crystals; its solubility is 2.7 kg/L of water at 100°C, 1.86 kg/L at 20°C, and 1.62 kg/L at 0°C. It can be formed by neutralization of the carbonate or hydroxide with hydrochloric acid.

Cesium perchlorate [13454-84-7], $CsClO_4$, mol wt 232.35 and theoretical cesium content 57.2%, is a crystalline powder that decomposes at 250°C.

Cesium fluoride [13400-13-0], CsF, mol wt 151.90, theoretical cesium content 87.49%, has a melting point of 682–703°C and a boiling point of 1253°C. Cesium fluoride is an extremely hygroscopic, colorless, crystalline solid; it has a solubility of 3.665 kg/L of water at 18°C. Cesium fluoride is made by exactly neutralizing cesium hydroxide with hydrofluoric acid and evaporating the resultant solution to dryness at 400°C. Excess HF results in a bifluoride salt that does not decompose at 400°C, and carbonate in the starting material gives an alkaline product.

Cesium iodide [7789-17-5], CsI, mol wt 259.81, theoretical cesium content 51.2%, has a melting point of 621°C and a specific gravity of 4510 kg/m^3. It is colorless, crystalline, hygroscopic, and has a solubility of 0.74 kg/L of water at 20°C, and 1.6 kg/L at 61°C. It is formed by the neutralization of the hydroxide or carbonate using hydriodic acid.

8.4. Cesium Hydroxide. Cesium hydroxide [21351-79-1], CsOH, mol wt 149.91, theoretical cesium content 88.66%, is a colorless, crystalline, hygroscopic, anhydrous, lumpy solid, having a melting point of 272°C and a specific gravity of 3680 kg/m^3. It has a solubility of about 4 kg/L of water at 15°C and is sold both in the solid form and as a 50% solution. It is the strongest base known, and hot, concentrated cesium hydroxide rapidly attacks nickel and silver, which are often used as container materials for less reactive hydroxides. Cesium hydroxide solutions can be dehydrated in platinum at 180°C to give the monohydrate, and further dehydration at 400°C, in a vacuum, results in the anhydrous solid being formed. Carbon dioxide (qv) is absorbed rapidly from the air by both the solid and aqueous solutions of cesium hydroxide. Reaction of the solid hydroxide and carbon monoxide at atmospheric pressure and elevated temperature results in the formation of cesium formate [3495-36-1], $CsHCO_2$, cesium oxalate [18365-41-8], $Cs_2C_2O_4$, and the carbonate.

Cesium hydroxide monohydrate [35103-79-8], $CsOH{\cdot}H_2O$, mol wt 167.93, theoretical cesium content 79.14 wt%, is a colorless, hygroscopic, crystalline powder, having a melting point of 205–208°C and a specific gravity of 3500 kg/m^3. It is highly soluble, 8.6 kg/L of water at 15°C; similar to the anhydrous hydroxide, it is an extremely strong base.

8.5. Cesium Nitrate. Cesium nitrate [7789-18-6], $CsNO_3$, mol wt 194.91, theoretical cesium content 68.19 wt%, crystallizes from solution in well-defined, glittering, colorless, hexagonal prisms. It has a melting point of 414°C, a specific gravity of 3685 kg/m^3, and a solubility of 0.09 kg/L of water at 0°C, and 1.97 kg/L at 100°C. Cesium nitrate is prepared from the chloride by heating with excess nitric acid until a negative test for chlorides is obtained; the reverse conversion to chloride using excess hydrochloric acid is also possible. Cesium nitrate is an ideal salt for obtaining cesium free from other alkalies, as fractional crystallization from water effectively eliminates traces of lithium, sodium, potassium, and rubidium.

8.6. Cesium Oxides. Cesium forms a series of oxides, including cesium monoxide [20281-00-9], Cs_2O, mol wt 281.81, theoretical cesium content 94.32 wt%; the suboxides: cesium heptaoxide [12433-62-4], CsO_7, tetracesium oxide [12433-60-2], Cs_4O, heptacesium dioxide [12433-63-5], Cs_7O_2, and tricesium oxide [12433-59-9], Cs_3O; cesium peroxide [12053-70-2], Cs_2O_2; and cesium superoxide [12018-61-0], CsO_2. The suboxides are formed by incomplete oxidation of cesium metal or by treating cesium monoxide with cesium metal. Cesium monoxide can be formed by direct combination of the elements or by thermal decomposition of the suboxides in the form of polycrystalline laminated plates, which are lemon yellow at $-80°C$, orange-yellow at room temperature, and cherry red $>180°C$. The crystal structures of both Cs_2O and Cs_3O have been determined by single-crystal X-ray studies (37).

Partial oxidation of cesium metal changes its color from silver-white to golden yellow; further oxidation using dry oxygen gives a black reaction product which, in the presence of oxygen at 330°C, changes to the bright yellow superoxide, CsO_2. Thermal decomposition of this product at 280–360°C yields the peroxide, without the formation of intermediate sesquioxide; further decomposition results in the monoxide (38).

8.7. Cesium Permanganate. Cesium permanganate [13456-28-5], $CsMnO_4$, mol wt 251.84, theoretical cesium content 52.77 wt%, has a specific gravity of 3597 kg/m^3, decomposes at 320°C, and is relatively insoluble at $\sim$1 g/L of water. It is prepared in the Carus process by precipitation through the reaction of hydrated cesium alum with potassium permanganate (29). It can be reduced to cesium chloride or cesium carbonate using a reducing agent such as methanol.

8.8. Cesium Sulfates. Cesium sulfate [10294-54-9], Cs_2SO_4, mol wt 361.87, theoretical cesium content 73.46 wt%, forms colorless, rhombic, or hexagonal crystals and has a melting point of 1010°C and a specific gravity of 4243 kg/m^3. It can be obtained by adding a hot solution of barium hydroxide to a boiling solution of cesium alum until all the aluminum is precipitated. This equivalence point is well indicated by spot-testing for alkalinity using bromthymol blue, which has pH 7.6. Filtration yields a filtrate barren of aluminum hydroxide and barium sulfate, and the cesium sulfate is then obtained by concentration and recrystallization from water.

Cesium aluminum sulfate [7784-17-0] (cesium alum) $Cs_2SO_4{\cdot}Al_2(SO_4)_3{\cdot}24H_2O$, mol wt 1136.39, theoretical cesium content 23.39 wt%, has a melting point of 117°C and a specific gravity of 1970 kg/m^3. It is the least soluble of the alkali alums, having a solubility of $\sim$0.32 kg/L of water at 100°C but only 0.015 kg/L at 50°C. It therefore crystallizes first from aqueous mixed solutions of the alkali alums, as colorless, octahedral crystals and can readily be separated completely from lithium, sodium, and potassium alums by fractional distillation; the relative solubility of rubidium alum is such, however, that multiple-stage fractional crystallization is required to effect a separation. Cesium alum is the digestion product of pollucite in sulfuric acid and is one of the starting points for the production of cesium compounds.

8.9. Other Cesium Compounds. Cesium acetate [3396-11-0], $CsOOCCH_3$, mol wt 191.95, theoretical cesium content 69.24 wt%; cesium trifluoroacetate, CF_3COOCs, mol wt 245.93, theoretical cesium content 54.04 wt%; cesium–precious metal compounds such as cesium dicarbonyltetrachlororuthenium, [22594-81-6] $Cs_2RuCl_4(CO)_2$, mol wt 564.71, ruthenium content of 17.9 wt%, a yellow crystalline powder; and cesium tetrachlorogold [13682-60-5], $CsAuCl_4$, mol wt 471.7, gold content of 41.8 wt% a yellow powder; are all known.

9. Handling, Storage, and Shipment

Because of the high reactivity of cesium metal, special precautions are required for its storage, transportation, and use. Small quantities are usually contained in evacuated glass ampuls, larger quantities in stainless steel containers that are themselves contained in an outer packing, ensuring that the metal is kept from moisture or air. Most cesium compounds are hygroscopic, especially the halides, and must therefore be stored dry. Other precautions that must be taken depend on the anion. Most products are sold in polyethylene bottles inside of clamping ring steel drums.

The toxicology, occupational health hazards, and transportation regulations of cesium compounds result from the anion rather than the cesium cation. Producers and distributors provide an MSDS as well as detailed shipping requirements for each product.

10. Economic Aspects

The cesium market is very small. Most current applications require relatively small quantities of cesium and hence annual world production of cesium and compounds is estimated to be on the order of 375 t of cesium chloride equivalents. As a result, there is no official market price. However, several companies publish prices for cesium and cesium compounds. The prices have remained stable for several years (18). The per unit prices for the metal or compounds purchased from these companies varies with the quantity and quality of material purchased. As an example, one company offered 1-g ampuls of 99.98%-grade cesium metal at $50.00. The price for 100 g of the same material was $1370 (18). Technical grade compounds were priced in the range of $20–30/kg.

The United States depends on imports for 100% of its needs (18).

11. Standards and Analytical Procedures

The determination of cesium in minerals can be accomplished by X-ray fluorescence spectrometry or for low ranges associated with geochemical exploration, by atomic absorption, using comparative standards. For low levels of cesium in medical research, the proton induced X-ray emission technique has been developed (39).

Cesium metal and cesium compounds are produced and marketed in a variety of grades, eg, from 99% for technical grades to as high as 99.999% for ultrapure compounds.

Analysis and purities of the metal or compounds are determined by difference, subtracting the sum of the analyzed levels of all impurities from 100%. Analysis of impurity levels is carried out by the most appropriate technique, which may include spectroscopy, atomic absorption, and photometry.

12. Health and Safety Aspects

The cesium ion is more toxic than the sodium ion but less toxic than the potassium, lithium, or rubidium ion. No threshold limit value is stated for cesium or cesium chloride; the TLV for cesium hydroxide is 2 mg/m^3. The oral LD_{50} of cesium chloride for mice is 2300 mg/kg, and for cesium flouride is 400–700 mg/kg (40).

The hydroxide, which is one of the strongest know bases, can be formed from moisture resulting in alkaline toxic effects. Cesium has been studied as indicated medically in depressive disorders (41). Because of the small-scale production of cesium products, no significant environmental problems have been encountered (18).

13. Uses

The number of commercial uses of both cesium metal and its compounds has grown significantly since the early 1980s. Cesium compounds are used in research and development, and commercially in electronic, photoelectric, and medical applications (18).

13.1. Electronic Applications.

Electronic applications make up a significant sector of the cesium market. The main applications are in vacuum tubes, photoemissive devices, and scintillation counters (see ELECTRONIC MATERIALS).

Vacuum Tubes. In the manufacture of vacuum tubes for use in polarized ion sources, vaporized cesium is used as a getter for residual gaseous impurities in the tube and as a coating to reduce the work function of the tungsten filaments or cathodes of the tube. The cesium vapor is generated by firing, at ~850°C within the sealed and evacuated tube, a cesium chromate pellet and zirconium (12) (see VACUUM TECHNOLOGY).

$$4\ Cs_2CrO_4 + 5\ Zr \longrightarrow 5\ ZrO_2 + 8\ Cs + 2\ Cr_2O_3$$

Photoemissive Devices. The development of the silver–oxygen–cesium photoemitter, which converts photons into free electrons, resulted in commercial exploitation of photoemissive devices; the first important use was the reproduction of sound from film, followed by such devices as the photomultiplier, iconoscope, image orthicon, and optical character recognition devices (41) (see IMAGING TECHNOLOGY; PHOTODETECTORS). The Ag–O–Cs photoemitter has relatively low sensitivity, and most photoemitters are constructed using intermetallic compounds such as antimony tricesium [12018-68-7], $SbCs_3$, and the bialkali K–Cs–Sb, rather than alloys. In the photomultiplier tube, cesium is used both in the photocathode and also as a secondary emission material in the dynode. Photomultipliers are used in a wide range of equipment, including pollution and radiation monitoring equipment; scientific, military, and medical equipment; and gamma-ray cameras.

Scintillation Counters. Cesium iodide and cesium fluoride are used in scintillation counters, which convert energy from ionizing radiation into pulses of visible light. Such units have special application in the fields of medical diagnostics, oil and mineral exploration, analysis, and space, military, and nuclear physics research (42). Thallium activated cesium iodide monocrystals have been incorporated in a synchrotron for detecting high energy gamma rays (43). Cesium iodide and cesium bromide are used for the preparation of lenses, prisms, and cuvettes for use in infrared spectrometers, especially in the 500–550 nm range (see INFRARED AND RAMAN SPECTROSCOPY).

Other. Alkali chlorochromate compounds, including cesium chlorochromate, $CsCrCl_4$, are ferromagnetic substances being studied for potential application in optically read computer memory devices. Cesium has also been used in vapor glow lamps (44), vapor rectifiers, and high energy lasers (qv) (45).

13.2. Biotechnology and Medical Applications.

Cesium chloride, and to a lesser extent the other halides, cesium trifluoracetate and cesium sulfate, are used in the purification of nucleic acids (qv), ie, RNA and DNA, viruses, and other macromolecules (46). Molecules are separated according to density after being subjected to a centrifugal density gradient. In medicine, cesium salts have been considered both as an antishock reagent following the administration of arsenical drugs, though a contraindication is the disturbance to heart rhythm (47), and for the treatment of epilepsy.

The isotope ^{134}Cs, $t_{1/2} = 2.05$ year, emits a β particle and is useful in radioautography (48). Research into the use of the stable ^{133}Cs isotope and the positron-emitter ^{132}Cs, $t_{1/2} = 6.47$ day, as well as ^{131}Cs, $t_{1/2} = 9.7$ day, for cancer treatment has been carried out (49), although these processes have not yet been commercialized.

13.3. Chemical Applications.

Cesium metal is used in carbon dioxide purification as an adsorbent of impurities; in ferrous and nonferrous metallurgy (qv) it can be used as a scavenger of gases and other impurities.

The performance of many metal-ion catalysts can be enhanced by doping with cesium compounds. This is a result both of the low ionization potential of cesium and its ability to stabilize high oxidation states of transition-metal oxo anions (50). Catalyst doping is one of the principal commercial uses of cesium. Cesium is a more powerful oxidant than potassium, which it can replace. The amount of replacement is often a matter of economic benefit. Cesium-doped catalysts are used for the production of styrene monomer from ethyl benzene at metal oxide contacts or from toluene and methanol as cesium-exchanged zeolites; ethylene oxide; ammonoxidation, acrolein (methacrolein); acrylic acid (methacrylic acid); methyl methacrylate monomer; methanol; phthalic anhydride; anthraquinone; various olefins; chlorinations; in low pressure ammonia synthesis; and in the conversion of SO_2 to SO_3 in sulfuric acid production.

A growing use of cesium compounds is in the field of organic synthesis, replacing sodium or potassium salts. Various cesium compounds are highly soluble in polar solvents. These compounds do not decompose as do many organic compounds, thus avoiding undesirable by-product formation. Additionally, the cesium component can be recovered and recycled. The use of cesium fluoride in esterifications is typical, eg, the synthesis of phenacyl esters (51); in the production of trialkyl phosphates, ie, a plasticiser (52); in polymerizations; and in the preparation of organoflourine compounds, such as ring fluorinated aromatics, by halogen exchange. In this latter case, it can be used either alone, as a catalyst to accelerate KF reactions, or in combination with calcium fluoride as a support reagent (53). Cesium carbonate can be used in intramolecular cyclizations; eg, cyclic oligoethers can be prepared utilizing the template effect of the cesium cation (54). Cesium hydroxide can be used for the synthesis of insoluble fatty acid esters and polyesters (52).

Molten (177–343°C) cesium hydroxide can be used in desulfurizing heavy oils. The hydroxide may be recycled by steam hydrolysis (55).

13.4. Energy Related Applications. Much research, with regard to the use of cesium in energy related processes, has resulted in little commercial application. The heightened awareness of the environmental degradation caused by fossil fuel power stations has resulted in increased research both into efficiency improvements for existing plants and into alternative power generation (qv) methods.

Cesium is ideally suited for use in magnetohydrodynamic (MHD) power generation. The metal can be used as the plasma seeding agent in closed-cycle MHD generators using high temperature nuclear reactors (qv) as the primary heat source. However, open-cycle MHD offers considerable potential for increasing the efficiency of fossil fuel fired power plants from 30–35% to 45–50%. Hot combustion gases are seeded using cesium oxide or cesium carbonate, potassium carbonate, or a mixture to form a highly conductive plasma that is accelerated through a magnetic field channel, ideally a superconducting magnet, and an electric current is generated at right angles to both the flow of plasma and the magnetic field. The off-gases thereafter pass to a conventional power generator. One of the significant potential side benefits of this process is the scrubbing of sulfur from the off-gases by the seeding material. Potassium carbonate is considerably cheaper but also much less effective than the cesium compounds; the use of a mixture of the salts has been proposed to be the best choice (56) (see PLASMA TECHNOLOGY).

MHD generated considerable interest in the 1960s and 1970s and by 1971, a 20 MW unit had been constructed in Russia. By 1986 a commercial-scale 500 MW plant was built at Ryazan. Interest elsewhere waned, but since the mid-1980s interest in the United States has again increased, resulting in plans to build pilot-plant versions (57).

One alternative method of generating electricity directly from a heat source is by the use of a cesium vapor thermionic convertor, which uses cesium to neutralize the space charge above a hot cathode that is emitting electrons toward a cooler anode. A nuclear reactor is required as the heat source because temperatures of ~1900°C are necessary (58). Cesium has also been considered as a working fluid for high temperature Rankine-cycle, turboelectric generators (59).

Cesium oxide has been mentioned as a coating in solar photovoltaic cells (qv) (see Solar Energy), and cesium hydroxide has been considered as a partial replacement of sodium or potassium hydroxide in alkaline storage batteries (qv) especially for use at low temperatures (60), although lithium is now preferred.

Ion engines are used in satellites for orientation control. Cesium is vaporized in a vacuum and ionized as it passes through a heated porous tungsten disk, the ions are accelerated by an electric field to $\sim$135 km/s and are neutralized by the injection of electrons and exhausted from the thruster. However, mercury-, xenon-, and argon-based ion engines are preferred.

13.5. Other Applications. The refractive index of silicate or borosilicate glass can be modified by the addition of cesium oxide, introduced as cesium nitrate or carbonate. Glass surfaces can be made resistant to corrosion or breakage by surface ion exchange with cesium compound melts or solutions. This process can also be used for the production of optical wave guides (61). A cesium–lithium–borate crystal can be used for frequency conversion of laser light (62).

Cesium metal is used for time standards based on the natural vibration of the ^{133}Cs atom, which oscillates 9,192,631,770 times/s, and in high precision oscillators to synchronize fiber optic telecommunication.

It has been suggested that cesium may be useful in the fixation of radioactive waste in a cesium-based glass and in detoxification procedures for fugitive ^{137}Cs emissions, such as at Chernobyl, Ukraine. Methods for the removal of cesium from radioactive waste liquids have been patented (63,64).

14. Cesium Isotopes

Naturally occurring cesium and cesium minerals consist only of the stable isotope ^{133}Cs. The radioactive cesium isotopes such as ^{137}Cs are generated in fuel rods in nuclear power plants (65).

Cesium isotopes can be recovered from fission products by digestion in nitric acid, and after filtration of waste the radioactive cesium phosphotungstate is precipitated using phosphotungstic acid. This technique can be used to prepare radioactive cesium metal or compounds. Various processes for removal of ^{137}Cs isotopes from radioactive waste have been developed including solvent extraction using macrocyclic polyethers (66) or crown ethers (67) and coprecipitation with sodium tetraphenylboron (68).

The radioactive isotope ^{137}Cs is important commercially in process controlinstruments and for sewage sludge sterilization. The isotope has a long half-life ($t_{1/2} = 30$ year); however, it must be well-shielded because of the high biological hazard. A method of separation of ^{131} Cs from barium has been patented (69).

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