

THE ALKALI METAL CESIUM AND SOME OF ITS SALTS¹

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The alkali group of metals in the order of increasing atomic weight comprises lithium, sodium, potassium, rubidium, and cesium. The metal cesium is the rarest one of the group and is also the most electropositive. It was discovered by Bunsen and Kirchhoff in 1860, by means of the spectroscope. Cesium was named by them after the Latin word "caesius," meaning "sky-blue," since the two prominent blue lines of its spectrum were most characteristic.

Cesium is found in very small amounts in a number of minerals: for example, in lepidolite, a lithia mica; in carnallite, a hydrous chloride of potassium and magnesium; and sometimes in beryl, a beryllium aluminum silicate. However, the most important source is the mineral pollucite, a silicate of aluminum and cesium which can contain as high as 42.5 per cent of cesium oxide on the basis of the formula $2\text{Cs}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 9\text{SiO}_2 \cdot \text{H}_2\text{O}$.

Breithaupt had found in 1846 two minerals constantly associated in small cavities in the Isle of Elba granite. He applied to them the names of Pollux and Castor, famous in mythology for their inseparable companionship. The cesium ore he called pollucite and its companion he called castorite. The latter is now known as petalite. It is a lithium aluminum silicate and is the same material in which lithium was discovered in 1817 by Arfvedson.

Pollucite in appearance is often clear and colorless, somewhat resembling quartz. Sometimes it is translucent to opaque with a fine-grained structure resembling massive beryl; occasionally it appears dull and almost gumlike externally. It is not easily recognized by casual inspection and probably many small deposits of it are passed unnoticed in the working of some granite pegmatite dykes for their various values. Pollucite has a hardness of 6.5 and a specific gravity of 2.88-2.90 when the material is high grade in quality.

In 1891 a single cavity of pollucite was found at Hebron, Maine, the

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dimensions of which were 3 ft. x 6 ft. x 1½ ft. It yielded about a pound of pollucite, which was described and analyzed by H. L. Wells (6). The ore occurred in fragments mixed with clay and associated with quartz and a cesium-bearing beryl. In appearance it was similar to the Elba mineral. The unusually large amount of it obtained from this source in Maine enabled Wells and Penfield to make some important researches upon the cesium trihalides.

Prior to the recent development during the past ten years (1) of the low voltage light of the Claude Neon type, (2) of the vacuum tube for radio work, and (3) of the photoelectric cell, cesium and its salts were regarded as laboratory curiosities. During 1926 and 1927 a demand for cesium developed from the manufacturers of radio tubes, and prices ranging up to \$15.00 per pound were reported for average-grade pollucite ore. This greatly stimulated prospecting activities and the demand was partially met by the small deposits uncovered in Maine. With the introduction on the market of the electric radio set and the consequent change in types of tubes, the demand soon fell off and the prices declined accordingly. Without doubt, the greatest strike of pollucite ore that has, to date, been removed from the earth's crust was found at the Tin Mt. Mine near Custer in the Black Hills of South Dakota. During the fall of 1927 this mine, owned and operated by the Maywood Chemical Works of Maywood, New Jersey, was opened for the primary purpose of developing lithium ore reserves for that Company. In the course of development work, consisting principally in the drilling of underground prospecting tunnels, at least four separate and distinct "pocket" formations of pollucite ore were discovered within a radius of 75 ft. Mining operations at Tin Mt. were discontinued in 1930 and to date have not been resumed. In all, over 100,000 lb. of cesium ore have thus far been obtained from this source. It has varied considerably in quality and some lots, being so altered in ages past by the geologic leaching of their alkali value, have run as low as 1 per cent cesium oxide. However, considerable ore with a cesium oxide content as high as 32 per cent was found. This Tin Mt. mine, a granite pegmatite deposit, has been described in the literature by G. M. Schwartz (5), Joseph P. Connolly (1), and others.

Pollucite, being a type of silicate mineral that is decomposable by mineral acids, is best processed for its cesium value by the direct treatment of the finely powdered ore with either hydrochloric or sulfuric acid, the choice depending somewhat upon the ultimate salt desired as finished product. The original methods for the extraction and purification of cesium from pollucite are largely the work of H. L. Wells. The essentials of his procedure consist in extracting the mineral with concentrated hydrochloric acid, dehydrating the silica in the extract, and precipitating

the cesium values either as cesium lead chloride ($2\text{CsCl}\cdot\text{PbCl}_4$) by the addition of lead nitrate (7), or as cesium antimony chloride ($3\text{CsCl}\cdot 2\text{SbCl}_3$) using antimony chloride (9). The use of the latter as a specific reagent for the precipitation of cesium salts had first been applied by Godeffroy (2). The lead chloride method had been devised by Wells, but in dealing with the crude extracts from pollucite ore it was later discarded because he found that while it was very convenient and efficient for removing small quantities of cesium from all sorts of solutions, it was inconvenient in cases where large amounts of cesium were concerned. Having obtained the double salt of cesium antimony chloride, Wells decomposed it either by suspending it in water and passing in hydrogen sulfide, which procedure he admitted was a slow and laborious operation, or he precipitated the antimony from the double salt by the addition of ammonium hydroxide. This produced large quantities of ammonium chloride, the removal of which was a serious drawback, not only because it was a very slow operation but because it introduced the danger of losing appreciable quantities of cesium chloride in the subsequent removal of the ammonium chloride by volatilization. Wells eliminated this shortcoming by converting the chlorides to nitrates by the addition of nitric acid and then entirely destroying the ammonium salts present by heating the solution until there was no further evolution of gas. The nitrates were then converted to the carbonates by adding two parts of oxalic acid and evaporating to dryness. On subsequent ignition the cesium oxalate was broken down completely at red heat into cesium carbonate, which was then dissolved in water, and separated by filtration from the insoluble traces of iron, aluminum, and antimony together with the carbon formed in the ignition. In this manner he finally obtained the cesium carbonate in pure form.

In 1924 Lenher, Kemmerer, and Witford (4) made some modifications in the Wells procedure of extracting the cesium values from pollucite. One change consisted in extracting the dry residue, obtained in the silica dehydrating operation, with hydrochloric acid of a concentration that would render least soluble the cesium antimony chloride subsequently formed. This concentration in their experience was 3 normal acid. They also hydrolyzed the cesium antimony salt by boiling with water, thereby directly obtaining a product which contained only small quantities of antimony along with traces of iron and aluminum, once the bulk of the precipitated antimony salts had been removed by filtration. They finally obtained the cesium in the form of pure cesium carbonate, after converting the chloride to the nitrate and then to the oxalate according to the procedure of Wells, the yield of carbonate from the pollucite ore used by them amounting to 37 per cent.

In the problem of the large scale extraction of cesium values from many

tons of the pollucite ore found at Tin Mt., the finely divided ore was treated with hydrochloric acid, the mass was leached with considerable water, the resulting solution was concentrated to a strength of about 15 per cent hydrochloric acid, and the double salt of cesium antimony chloride was precipitated by the addition of antimony chloride. The precipitate so obtained was decomposed by boiling water and the filtered solution of the chlorides was then treated with ammonia and ammonium carbonate to remove aluminum, iron, antimony, and calcium impurities. The solution so obtained was acidified with hydrochloric acid, and the cesium values again precipitated in the form of the double cesium antimony chloride, thereby eliminating the bulk of the very troublesome ammonium salts. The double salt was again decomposed with boiling water, the filtered solution was evaporated to dryness, and the small amounts of ammonium salts present were volatilized by controlled heating. The crude chlorides were then dissolved in water, acidified, and the small amount of residual antimony was removed by the addition of hydrogen sulfide. The cesium chloride was next obtained in pure form by fractional crystallization from aqueous solution, the small amounts of lithium, sodium, potassium, and calcium impurities being thereby eliminated. A cesium chloride exceeding 99.9 per cent in purity was obtained by this procedure.

The cesium values can also be obtained from pollucite ore by treatment with 50 per cent sulfuric acid. The resulting mass is diluted with water and filtered at a temperature approximating 100°C. When this solution is cooled, the cesium values are directly obtained in the form of well-defined crystals of cesium alum, because in the first place the ore contains the cesium with enough aluminum present to form the alum and because the solubility of the cesium alum in the dilute acid solution diminishes markedly as the temperature is lowered from 100°C. to even 50°C. The amount of acid originally used and the extent of the subsequent dilution with water depend somewhat upon the quality of the ore at hand. The extent of the cooling of the filtered acid liquor and the possibility of need for further concentration to obtain one or more extra crops of alum are also dependent upon the grade of ore, since the fractionation of the various alums is altered by the presence of varying amounts of other salts. In any event, the cesium alum being most insoluble tends to crystallize out first and is followed in order of solubility by the alums of rubidium, potassium, and sodium. The cesium alum crystallizes in well-defined octahedral crystals, and like all the other members of the alum group contains twenty-four molecules of water of crystallization. The alum was early recognized as one of the compounds of cesium that offered opportunities for original work, as is evidenced by the studies of Redtenbacher in 1865, Setterberg (1881), Lock (1901), and Hart and Huseton (3) in 1914. Data

concerning the solubility of cesium alum in water at various temperatures, as given in the literature, are rather confusing, owing probably to the use of material of varying purity. We have found that pure cesium alum ($\text{Cs}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) has a solubility of about 32 parts in 100 parts of water at 100°C ., that at 50°C . the solubility drops to less than 1.5, and that at 5°C . only 0.25 part remains in 100 parts of water.

With cesium chloride as starting material, the nitrate and carbonate can be made according to the method of Wells as previously outlined. Cesium chromate can be made from the chloride by the use of pure silver chromate. Cesium sulfate, however, is not readily prepared in pure form from cesium chloride and an excess of sulfuric acid, on account of the marked stability of cesium acid sulfate at the fusion point. The usual procedure for eliminating small amounts of acid sulfate from the normal alkali sulfates is to fuse with small amounts of ammonium carbonate. Even when very large excesses of ammonium carbonate are used, the cesium sulfate still contains a small amount of the acid sulfate. This is readily removed by dissolving in water and adding cesium hydroxide to exact equivalence. The pure normal sulfate can then be crystallized from the aqueous solution.

Cesium alum is, in many cases, an ideal salt for preparing various salts of cesium. For example, cesium sulfate can be readily made by adding a hot solution of barium hydrate to a boiling solution of the cesium alum until all of the aluminum is precipitated. This point is very well indicated by spot-testing for alkalinity with bromothymol blue (pH 7.6). The filtered solution should give no test for either aluminum or barium, and pure cesium sulfate is then readily obtained by concentration. Cesium hydroxide can be prepared from a solution of the sulfate by the addition of a boiling solution of barium hydroxide to the point of exact equivalence. From the filtered cesium hydrate solution, the carbonate can be made by the introduction of carbon dioxide. In preparing cesium carbonate from the sulfate, experience in our laboratory shows that it is not good practice to add the barium hydroxide solution in excess, expecting to remove the excess barium later as barium carbonate along with the barium sulfate precipitate previously formed. Under these conditions the finished cesium carbonate solution will not be free of sulfates, in spite of the fact that such was the case previous to the introduction of the carbon dioxide.

Cesium, the most electropositive of all the elements, has a silvery white appearance when pure. It has a specific gravity of 1.9, melts at 28.5°C ., and boils at 670°C . It ignites spontaneously in the air at room temperature, this action probably being due to the presence of traces of moisture. It also ignites spontaneously in *dry* oxygen at room temperature. In contact with traces of air left in highly evacuated glass tubes it gradually

takes on a golden yellow color, and in the presence of more than minute traces of air it rapidly becomes black. When cooled to the temperature of carbon dioxide snow the metal is stable when exposed to air for short periods of time. The metal can be stored for long periods of time and its characteristic silvery appearance maintained by distilling it under a vacuum of 0.001 mm. of mercury into a glass apparatus consisting of two bulbs joined by a narrow open constriction. After the cesium has remained in one of the bulbs for several months under high vacuum and has scavenged the last traces of air from the glass interior, it is then distilled into the second bulb, and the first bulb is removed by means of a blowpipe. Metallic cesium reacts with water at ordinary temperature with explosive violence. In contact with ice, the metal generates hydrogen at all temperatures above -116°C .

Cesium metal can be prepared by the method of Erdmann and Kothmer, which consists in heating the hydroxide in an iron tube in an atmosphere of hydrogen with an excess of magnesium as the reducing agent. The method of Setterberg, by the electrolysis of the cyanide, produces a low yield which can be improved by using a mixture of 4 parts of cesium cyanide and 1 part of barium cyanide. In our opinion the metal can best be made by heating cesium chloride and metallic calcium in a nickel tube under a vacuum of 0.001 mm. to about 675°C . At this temperature the reaction ($2\text{CsCl} + \text{Ca} = 2\text{Cs} + \text{CaCl}_2$) takes place quietly and the metal can be distilled into a glass receiver. On redistillation under high vacuum the metal can be obtained in a high state of purity with a yield of 90 per cent.

Metallic cesium is used as such in the manufacture of photoelectric cells. However, in its use in radio and other low voltage tubes, where its function consists not only in scavenging the last traces of air left in the tube, but also in supplying positive ions at the surface of the filament, the metallic cesium is formed within the tube itself. This is done by loading so-called "getter" cups contained within the tube with different salts of cesium and various reducing agents. At the proper time the metal "getter" cup is heated by means of an induced current to the desired temperature for bringing about the reduction to metallic cesium. Cesium salts such as the chloride, carbonate, nitrate, and chromate mixed with various reducing agents such as magnesium, magnesium and graphite, barium-calcium alloy and others have been used with varying success, manufacturers keeping the details more or less secret.

In analyzing cesium-bearing silicates, such as pollucite and various micas, the alkalis can be obtained in the form of chlorides by the method of J. L. Smith. The perchlorate method leaves little to be desired in sharply separating the soluble perchlorates of lithium and sodium from

the insoluble perchlorates of potassium, rubidium, and cesium. Since there are no truly specific reagents for potassium, rubidium, or cesium ions in the presence of one another the remainder of the problem is not so simple. In our experience, where cesium is the main constituent, the double precipitation of the double cesium antimony chloride coupled with spectroscopic examination by comparison with known mixtures gives good results.

From the foregoing description of the substantial cesium ore deposit uncovered in 1927 in South Dakota, it should be quite evident that during the past ten years there has been no shortage of cesium ore supplies. The demand, however, for finished cesium salts has been very limited, especially since 1929. Considerable research activities have been carried on by various concerns but to date, to the best of our knowledge, there has been no real commercial demand for cesium products. The small amounts required coupled with the exacting specifications for purity of products—some impurity limits being set as low as 0.001 per cent—have resulted in the price remaining high. With increased demand there is every reason to believe that present prices could be decreased very appreciably.

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