[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION OF VERY PURE BARIUM AND STRONTIUM

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The difficulties involved in the preparation and handling of metallic barium and strontium are such that few specimens of these elements of a high degree of purity have ever been secured. Determinations of the values of the several physical and electrical constants of these metals have consequently either been made upon poor samples of material or else have not been made at all. It was with the object of producing the very pure metal required in such measurements in a form in which it could be indefinitely preserved and readily transferred from vessel to vessel that this investigation was undertaken.

Glascock[2] by electrolysis of a fused salt secured a product containing about 90% of strontium metal. Guntz[3] and his students in an extended series of investigations were able to develop two methods, applicable to both barium and strontium, which gave a product containing 97–99% of the metal. The second of these methods, employing the reaction of the alkaline earth oxide with magnesium or aluminum and subsequent distillation to separate the desired metal, has been used by several more recent investigators[4] with about the same results.

Since there seemed no reason why further refinement of this method could not be made to yield a product of the desired purity with a minimum of effort, it was adopted.

Materials.—The nature of the method requires that the reacting materials shall be free from any impurity having a vapor pressure comparable with that of the alkaline earth metal in question. To this end oxides of barium and strontium were prepared by dehydrating[5] the corresponding hydroxides which had been several times recrystallized and centrifuged. The oxide thus prepared was partially converted to peroxide by heating with oxygen at about five atmospheres' pressure. Both dehydration and conversion to peroxide were carried out in the same iron bomb. Especial care was exercised to secure aluminum free from the more volatile elements such as zinc. A good grade of commercial product was found to be satisfactory.

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[2] Glascock, THIS JOURNAL, 32, 1222 (1910).

[3] Guntz, *Ann. chim. phys.*, [8] **4,** 5 (1905); **10,** 437 (1907); *Compt. rend.*, **83,** 872 (1901); **141,** 1240 (1905); **143,** 339 (1906). Guntz and Roederer, *Bull. soc. chim.*, [3] **35,** 503 (1906).

[4] Dafert and Miklanz, *Monatsh.*, **34,** 1685 (1913). Biltz and Hüttig, *Z. anorg. Chem.*, **114,** 241 (1920). Ruff and Hartmann, *ibid.*, **133,** 29 (1924).

[5] Johnston, *Z. physik. Chem.*, **62,** 347 (1908).

Reaction.—The conditions found most favorable for a smooth and nearly complete reaction were roughly those originally employed by Guntz. The peroxide content of the oxide should be about 10% and the aluminum in the form of a coarse powder. The reaction is, however, caused to take place in an auxiliary vessel and the cooled product is transferred to the distilling vessel. This avoids the rather considerable contamination of the walls of the vessel and the condenser by a deposit of the reacting materials which may be carried throughout the apparatus by the violence of the reaction, and is imperative when metal of high purity is to be produced by a single distillation. The reaction is started by striking an arc between iron or aluminum electrodes enclosed in the body of the reaction mass. No difficulty is experienced due to the reaction of the metal with the atmosphere as it is so completely enclosed in the mass of alumina produced that loss of metal is noticeable only after several days' exposure.

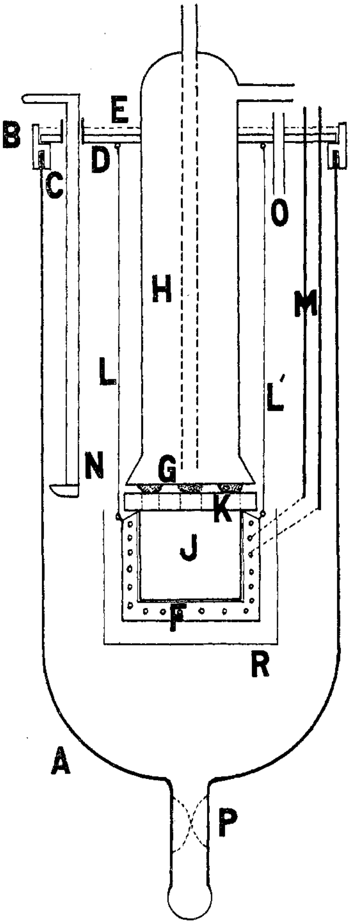

Fig. 1.

Distilling Apparatus.—The distilling apparatus which has been employed is represented in Fig. 1.

The outer tube A is of Pyrex glass, about 15 cm. in internal diameter by 45 cm. long. The brass ring at B was sealed to this tube by inverting, filling the groove at C with molten de Khotinsky cement, inserting the previously warmed tube and allowing to stand until cold. The brass plate D is cut to fit closely into the ring B and serves as the support for the furnace and condenser. When the whole assembly was in place the top of the apparatus was completely covered with a layer of de Khotinsky cement as shown at E. The tube O connects the vessel to the high vacuum line. The condenser tube H is so constructed that cold water circulates freely to the bottom. This large metal tube, soldered to the brass plate which is in good contact with the brass ring, serves to keep the several de Khotinsky seals from softening even when the furnace at F is kept at 1000° for hours at a time. The furnace F is a thin shell of fire brick grooved on the inside to permit the winding of 10–15 ohms of heating element. The crucible J is made of the purest iron obtainable and of such a size that it slides easily into the furnace, in this case about 5 cm. high by 4.5 cm. in diameter. The cover K is made to fit tightly on the crucible and contains a number of small holes, 6 to 7 mm. in diameter, which cause the metal being distilled to deposit on the condenser in small pellets, as indicated at G. The whole assemblage is suspended by the two fine wires L and L′

so that the crucible top is 3–4 mm. below the bottom of the condenser. The wires L and L′ are so arranged that they may be burned off by sending a heavy current through them, thus allowing the furnace to fall to the side where it remains suspended by the lead-in wires M. The device N is constructed so that when it is rotated it will disengage the small pellets of metal from the condenser. These pellets, the furnace having been allowed to swing aside, are thus permitted to fall into the tube P. The bottom of this tube is blown out sufficiently thin so that when the tube has been sealed off as indicated by the dotted line this thin end may be crushed by allowing the tube to strike on it after having been dropped through a short distance. This permits the sample of metal to be transferred to another evacuated vessel while it is still sealed in the same vacuum in which it was distilled.

Distillation.—Immediately previous to being introduced into the distillation apparatus the mass of alumina containing the metal was ground to the size of coarse sand and the very fine particles were removed. The vessel was then sealed and evacuated as quickly as possible. The furnace was warmed gradually during the process of evacuation in order that a large part of the adsorbed gases might be removed before the temperature of distillation was approached. This usually took from six to ten hours, as the distillation was never commenced until the pressure could be maintained at 10^{-4} mm. of mercury or lower with the diffusion pump running. When this condition was reached the heating current was increased until the furnace reached 950°; at this temperature a crop of pellets of metal was produced in about twenty minutes. It was found that radiation loss at this temperature could be very appreciably cut down by suspending a roughly polished metal vessel, indicated at R of Fig. 1, around the furnace. After the furnace had cooled it was allowed to swing to one side and the metal was removed from the condenser and sealed off as previously indicated.

Results.—About 20 g. each of barium and of strontium was prepared by this method. In almost every case the pellets of metal exhibited a surface which was silver-white and beautifully crystalline, often displaying tufts of crystals which resembled highly magnified snow flakes. Both metals are quite soft and malleable, about as hard as metallic sodium. Barium is spontaneously inflammable in moist air and hydrogen and tarnishes rapidly in pure dry carbon dioxide. Strontium is only slightly less reactive.

Several of the samples of barium taken at random and analyzed by the sulfate method showed a purity always better than 99.9%. While no samples of strontium were analyzed there is every reason to believe that it could not have been less pure.

This method would seem to be quite applicable to the purification of the better commercial grades of calcium and magnesium when small amounts of metal only are desired.

Summary

1. A method is described for preparing and transferring very pure samples of the alkaline earth metals.

2. A design of apparatus is given.
3. Some of the properties of pure barium and strontium are enumerated.

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BARIUM AND STRONTIUM AMALGAM ELECTRODES

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In a determination of the electrode potentials of barium and strontium by a method analogous to that employed by Lewis and his coworkers[2] in their determinations of the potentials of the alkali metals, it is necessary to know the potential of some amalgam of the metal against a standard electrode in an aqueous solution of the appropriate salt. The desirability of employing an amalgam of definite, constant and easily reproducible composition whenever measurements involving an amalgam electrode are made is entirely obvious. It has been pointed out[3] that these requirements are satisfied when a two-phase amalgam is used. A 0.1 M solution of a chloride with the standard calomel electrode is quite satisfactory for use with such an amalgam. Accordingly, measurements of the electromotive force of the following two cells have been made,

$$\text{Ba (2-phase amalgam), } BaCl_2(0.1\ M)\text{, HgCl, Hg} \qquad (1)$$

$$\text{Sr (2-phase amalgam), } SrCl_2(0.1\ M)\text{, HgCl, Hg} \qquad (2)$$

Design of Electrode Vessels.—Since no entirely satisfactory vessel has been described for use with amalgams which are as concentrated and consequently as reactive as are the two-phase amalgams, an extended investigation of this subject has been made.

The simple type of "dropping electrode" originally devised by Lewis and Kraus[2a] and since employed with various modifications by several other investigators is suited for use only where a continuous stream of dilute amalgam containing no solid phase may be kept running throughout a determination. When it becomes desirable to continue measurements with the same electrode for many hours either the quantity of amalgam which is necessary becomes very large and the apparatus unwieldy, or the flow of amalgam must be made intermittent. In the latter case the difficulty of preventing the solution from creeping in between the amalgam and the glass wall of the dropper tip increases rapidly with the concentration of the amalgam and with the time between renewals of the amalgam surface. When solution becomes trapped in this way between the amalgam and the vessel, reaction occurs which not only gives rise to fluctuating and erroneous

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[2] (a) Lewis and Kraus, THIS JOURNAL, **32,** 1459 (1910). (b) Lewis and Keyes, *ibid.*, **34,** 119 (1912); (c) **35,** 340 (1913). (d) Lewis and Argo, *ibid.*, **37,** 1983 (1915).

[3] (a) Gerke, THIS JOURNAL, **44,** 1686 (1922). (b) Danner, *ibid.*, **44,** 2837 (1922).