$$\text{RbCl (CsCl)} + \tfrac{1}{2}\,\text{Ca} = \tfrac{1}{2}\,\text{CaCl}_2 + \text{Rb (Cs)}$$

<div style="text-align:center">

120.9   (168.4)   20.0   55.5   85.5 (132.9)

</div>

This method, proposed by Hackpill, uses the apparatus shown in Fig. 262. A weighed amount of RbCl (CsCl) is thoroughly pre-dried in an oven at about 150°C and mixed with the required amount of Ca turnings. An iron insert crucible b is filled with the mixture and stoppered with a plug c made of fine steel wool. A ratio of 10 g. of RbCl (15 g. of CsCl) to 8 g. of Ca has proven satisfactory. The apparatus (Fig. 262) with a reaction vessel 30-35 mm. in diameter, will hold a maximum of about 35 g. of RbCl (50 g. of CsCl), together with the appropriate amount of Ca.
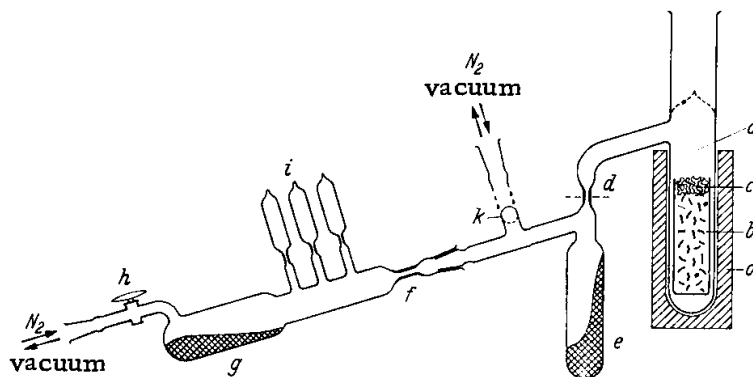

Fig. 262. Apparatus for preparation of metallic rubidium (or cesium) by reduction of the chloride with calcium.

After reaction vessel a has been opened, the filled crucible is placed in it and the vessel sealed directly above the side tube (dotted line in figure), leaving as little dead space as possible. The reaction vessel is placed inside the heater o and its top is wrapped as well as possible in asbestos wool, to prevent cold spots where later on the alkali metal vapor could condense. Heating under high vacuum is then started. The temperature is checked with a thermocouple, protected by a thin ceramic sheath and inserted between the vessel wall and the heater. The thermocouple sheath must not touch the vessel wall and is prevented from adhering to the latter by a few tufts of asbestos.

As the temperature rises to 250°C, large quantities of gases are released from the mixture. It is sometime before the vacuum pump is able to remove these. During this time all glass parts of the apparatus, are uniformly heated by fanning with a gas flame. After 2-3 hours, when the evolution of gas subsides, the temperature is raised further until all of the alkali metal slowly distills into receiver e. The distillation lasts 2-3 hours. Toward the end the temperature in the reaction vessel rises to about 650°C. The reactor is then disconnected from the remainder of the apparatus by melt-sealing constriction d while vacuum is maintained. This must be done before the heating is shut off, since vessel a is deformed by heat and will usually break on cooling.

The crude metal is distilled from collector e, using a tubular heater. The liquid metal runs through the ground joint and through constriction f into the second receiver g. (The ground joint should be carefully greased to prevent grease spillover into the passage.) The temperature in this vessel is considerably lower and the vacuum higher than in the first distillation stage. If very pure, the twice distilled metal will not wet the glass walls. Receiver g is finally sealed off under vacuum at constriction f. It thus becomes free and can be tipped in such a way that the metal, melted with low heat, will flow into ampoules i attached on the side. The number and size of these ampoules can be varied as desired. The liquid metal filling the ampoules will solidify more rapidly if externally cooled with a piece of Dry Ice. The ampoules are finally filled with very pure N_2 through stopcock h and sealed off at the constriction points in their connecting tubes. If the ampoules are weighed before and when filled, the weight of the contents can be determined to 0.01 g.

Somewhat larger quantities of alkali metal can be prepared in a stainless steel reactor (Fig. 263). A steel pipe l (inside diameter about 38 mm.), is filled with the reaction mixture m, covered with a steel wool plug n and closed with a heavy steel cap. The latter is sealed on with a lead gasket covered with a very thin copper foil sheath to protect it against corrosion by the alkali metal vapor. Just as in the case of the glass apparatus, the upper part

of the reactor (including the cap) must be thoroughly insulated. The metal vapor condenses in the water-cooled section of the side arm pipe. The cooling should not be too intensive and the liquid metal should be able to flow (without solidifying) into the next part of the apparatus via ground joint *p*. This remaining part of the apparatus is made of glass and, beginning with constriction *d*, is identical to that shown in Fig. 262.
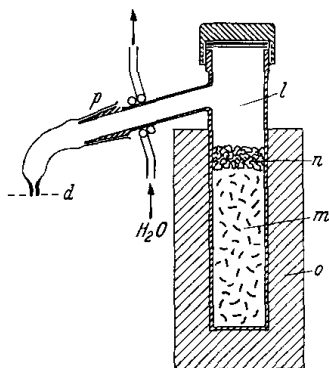

Fig. 263. Steel reactor for preparation of metallic rubidium (or cesium) by reduction of the chloride with calcium.

Such steel reactors allow processing 100 g. of RbCl, or 150 g. of CsCl in a single run. The yield of double-distilled metal is 90-98%.

REFERENCES:

L. Hackspill, Helv. chim. Acta 11, 1008 (1928).

W. Biltz, F. Weibke and H. Eggers, Z. anorg. allg. Chem 219, 119 (1934).

G. Brauer, private communication.

PROPERTIES OF ALKALI METALS

	Atomic weight	M.p.°C	B.p.°C	d (18°C)	Hardness (mohs)
Li	6.940	179.0	1336	0.534	0.6
Na	22.997	97.8	883	0.97	0.4
K	39.096	63.5	762	0.86	0.5
Rb	85.48	39.0	696	1.52	0.3
Cs	132.91	28.6	670	1.89	0.2

Very soft. Fresh surface is silver-white. Highly reactive. Immediately form hydroxide-carbonate crusts in air, usually accompanied in the case of Cs, by ignition. Water and alcohol are decomposed with liberation of H_2. (Storage, see below.) A2 structure type.

PURIFICATION OF ALKALI METALS BY VACUUM DISTILLATION

(See also the introduction to the section on Preparation of Alkali Metals by Reduction with Zirconium.)

Fig. 264 shows Brauer's apparatus for distilling Cs and Rb. Ordinary chemical glassware may be used. (However, according to Hevesy and Lögstrup, distillation of potassium requires Pyrex apparatus.) Tube *B* is slightly inclined. The ampoules are

melt-sealed to D in such a way that they are horizontal during the
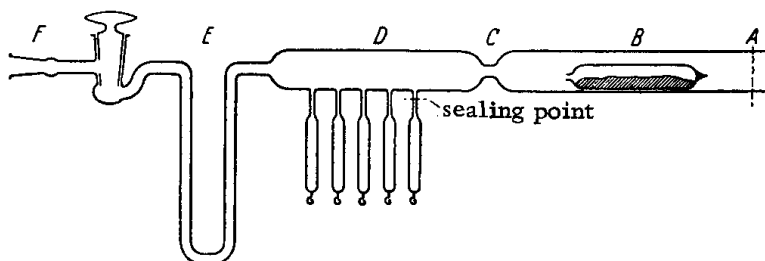early distillation stage. The apparatus is initially sealed off at

Fig. 264. Distillation of cesium (also rubidium,
potassium, sodium). Scale 1:7. In the actual ar-
rangement the ampoules, sealed to tube D, lie in
a plane perpendicular to that of the drawing; hence,
they remain horizontal during the distillation
and do not become prematurely filled with liquid
cesium. Tube B is likewise not quite coaxial with
D but is inclined slightly downward.

point A and evacuated by means of a mercury diffusion pump con-
nected to the ground glass joint F. the evacuation continues for
several hours, during which all of the apparatus, from A to E, is
dried by heating to 400-500°C. The system is then filled (through F)
with pure dry N_2. The tube end is broken off at A and a boat con-
taining benzine-covered cesium is introduced into tube B. The
metal should be free from any incrustations and washed in light
benzine (mineral spirits). The cesium in the boat must at all times
be protected either by the benzine layer or by a blanket of dry N_2,
or by both, as in the present example, where the benzine-covered
metal is pushed into the tube from which a stream of N_2 is issuing.
Following the insertion of the boat, the benzine is volatilized, B is
resealed at A, and the apparatus is evacuated to at least 10^{-4} mm.
Next, an electric oven is placed around B, reaching close to C, and
the metal is heated until all of it distills into D. Simultaneously,
the U tube E is cooled with liquid nitrogen or with Dry Ice-acetone
mixture to keep Hg and oil vapor away from the metal. Where
purity is not critical, the U tube can be dispensed with. Following
the distillation, the molten metal in tube D can be distributed
among the storage ampoules by rotation of the apparatus. After
cooling, the apparatus is refilled with N_2 and the ampoules are
sealed off.

If the metal must be distilled several times, several B tubes
are sealed on to D.

The vacuum distillation of Li is carried out according to method
of Remy-Genneté, using the same procedure as for Ca, Sr or Ba.

The apparatus in this case is a vertical tube. An iron crucible with the metal is inserted and the latter is allowed to distill from the crucible onto a cold finger hanging above. An apparatus of this type, improved by Ehrlich, is shown in Fig. 259 and is discussed under the distillation of Ca.

To prepurify the Li by removing the more volatile impurities, the first fraction is taken off by heating a fairly long time at a relatively low temperature. The apparatus is then cooled under vacuum and opened, and the first fraction of the metal is discarded. The actual distillation is then performed at a higher temperature. The charge should not be distilled to dryness. A residue of Li, containing high-boiling impurities, should be left behind in the crucible.

Lely and Hamburger describe a similar apparatus for the distillation of Na.

REFERENCES:

G. Brauer, Z. anorg. Chem. 255, 11 (1947).
P. Remy-Genneté, Ann. Chim. (10) 19, 263 (1933).
P. Ehrlich, see the section on Alkaline Earth Metals, Ca.
D. Lely, Jr., and L. Hamburger, Z. anorg. Chem. 87, 209 (1914).
G. von Hevesy and M. Lögstrup, Z. anorg. allg. Chem. 171, 3 (1928).

STORAGE AND HANDLING OF ALKALI METALS BEFORE USE

Lithium is stored in tightly closed vessels, completely filled with petroleum ether. Sodium is usually stored under kerosene. To clean the surface before use, the metal pieces are dried with filter paper, treated with absolute alcohol, and washed with pure petroleum ether. Potassium is usually also stored under kerosene. According to Wislicenus, Elvert and Kurtz, rolling potassium shot around under ether containing a few drops of alcohol will remove the brown crust from the surface. Rubidium and cesium are generally stored under paraffin oil, since they react rapidly under kerosene. Before use these metals are washed with petroleum ether or benzene, thoroughly predried with Na, to remove the oil. The solvents are evaporated in a current of dry CO_2 or removed under vacuum.

To remove oxide-hydroxide-carbonate crusts from Na and K, the following simple treatment has been suggested by Bornemann: a clean wire screen with 1-mm. openings, is inserted into a melting tube 50 cm. long and 15-20 mm. in diameter. The tube is sealed at one end and constricted in the middle to a diameter of 3-4 mm. The constricted section should be very short. The screen is bent to a hemispherical shape so that it fits snugly in the tube. It is pushed down the tube until it reaches the constriction. The tube

above the screen is half filled with freshly cleaned, well-dried pieces of Na or K. The tube is then sealed at a point about 20 cm. above the constriction. Over several hours the metal will have absorbed all the H_2O, O_2 and CO_2 from the air in the tube and will thus be essentially under an N_2 blanket. To check this, the metal is melted and left to resolidify, while the tube is horizontal (so that the metal will not run through the sieve). This procedure is repeated until the bright metal surface ceases to dull, even after a considerable time, indicating that the last traces of O_2 have been absorbed. The tube is then set vertically and its lower end heated to a temperature above the melting point of the metal so that the latter slowly melts. It gradually runs through the sieve, while the oxide, hydroxide and carbonate are left behind. Should the constriction become plugged, this spot is not heated. Instead, the flow is helped along by lightly tapping the tube against a soft support. At the end of filtration the metal is sealed in lower part of the tube by melting the constriction. No metal vapors must be allowed to form during sealing since they might attack the glass as well as cause pressure inside the tube.

A hopper designed by Zintl, Goubeau and Dullenkopf (Fig. 265) is used to fill small thin-walled glass spheres with high-purity Na (or K, etc.). The sphere is placed in the hopper and predried under vacuum for a long time. It is next weighed, together with its long, narrow capillary. Finally, it is put back into the hopper, with the capillary opening directed downward, as shown in the figure. The hopper is evacuated via ground joint adapter a. This takes a long time and high vacuum must be used. Simultaneously with the evacuation, the lower half of the hopper is heated to about 200°C on an oil bath to remove the water film lining the inner wall surface of the sphere. After cooling, pure dry N_2 is allowed to flow through a, the ground cap b is lifted momentarily, and a compact chunk of distilled Na (or K, etc.) is quickly inserted and placed as indicated in the figure. The metal should be as free from oxide as possible. The evacuation is immediately repeated. After a while, the heating on the oil bath is resumed in order to slowly melt the metal. Bright metal flows into the attached

Fig. 265. Filling of glass spheres with oxide-free alkali metal.

bulb c leaving behind all of the oxide in the form of a continuous film. Enough pure N_2 is then carefully let in to force the liquid metal into the sphere k so that its lower half is filled. Next, sufficient N_2 is pumped out to siphon the metal back into the capillary
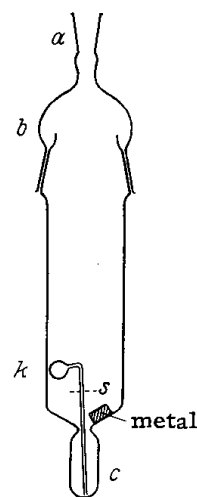
down to level s, thus forming a discontinuity. The metal will be retained in the sphere only if the latter has been thoroughly predried or it will empty as the N is pumped out. The metal is cooled until solid and the N pressure in the hopper is raised to 1 atm. The cap b is then removed and bulb c is immersed in a warm bath. As soon as the metal in c has melted, the sphere is withdrawn with glass hooks. This is done rapidly, while the capillary is still plugged with solid material. The capillary is then melt-sealed at the metal-free discontinuity close to the sphere. The filled sphere is weighed together with the cleaned capillary.

Sodium residues, which are still usable, are melted under toluene or xylene. Small amounts of residual sodium are rendered unreactive by being placed in portions in alcohol containing only a small amount of water.

REFERENCES:

W. Wislicenus, H. Elvert and P. Kurtz, Ber. dtsch. chem. Ges. 46, 3398 (1913).

G. Bornemann, Angew. Chem. 35, 227 (1922).

E. Zintl, J. Goubeau and W. Dullenkopf, Z. phys. Chem. A 154, 21 (1931).