LITHIUM CARBONATE FROM LEPIDOLITE

Lepidolite contains 1.2-6% (average 4-5%) LiO₂. According to a patent (Metallbank, Metallurgische Ges. A.G.), lepidolite is converted to Li₂CO₃ (and LiF or Li₃PO₄) in the following way.

Lepidolite is decomposed with concentrated H₂SO₄ and is then well calcined to decompose aluminum and iron sulfates. The aqueous extract of the roasted material contains impurities composed of salts of Al, Fe, Mg, Mn, etc. Most of these are separated by treatment with lime and calcium hypochlorite (to oxidize Mn). This purified liquor contains, in addition to Li and K sulfates (e.g., 6.6 g. of lithium/liter), traces of other salts such as CaSO₄ and occasionally MnSO₄ and MgSO₄. For this reason, a concentrated solution (about 1%) of Li₂CO₃, LiF, or Li₃PO₄ is added to the liquor until a precipitate ceases to form. About 100-150 ml. of the carbonate solution is required per liter of liquor, depending on how well the latter was prepurified. It is better to precipitate the last traces of impurities with a lithium salt, rather than with some other alkali salt, because an excess of the former precipitating agent causes no loss of original Li.

The liquor is then repeatedly purified until the Li₂CO₃, precipitated on addition of pure K₂CO₃ and filtered, washed and dried, is of analytical priority. Since the solubility of LiCO₃ is very high, large quantities of Li are still present in the mother liquor. This solute can be precipitated as the phosphate or the fluoride. These salts will also be very pure. Needless to say, all the Li can be precipitated as pure phosphate or fluoride without going through the partial precipitation of the carbonate.

This method can also be used for the purification of technical grade Li salts contaminated with Ca, Mg, Fe, etc.

Solubility of Li₃CO₃ (0°C) 1.54; (20°C) 1.33; (100°C) 0.73 g./100 g. of H₂O.

Solubility of LiF (18°C) 0.27 g./100 g. of H₂O.
Solubility of Li₃PO₄ (25°C) 1 g./3360 g. of H₂O.

REFERENCES:


RUBIDIUM AND CESIUM CHLORIDES FROM CARNALLITE

Natural carnallites contain, on the average, 0.02% RbCl and 0.0002% CsCl. “Synthetic carnallites,” which are obtained as intermediates in the manufacture of potassium chloride through recrystallization of natural carnallite, have a much higher Rb and Cs content.

I. According to Jander and Faber, as well as Jander and Busch, the first step in the simultaneous production of RbCl and CsCl from synthetic carnallite is recrystallization of the latter. Thus, synthetic carnallite (6.5 g.) is boiled in 2.3 liters of water. The hot liquor (d. 1.3) is suction filtered on a Büchner funnel to separate the solid KCl precipitate. The residue is placed in a dish and treated with 400 ml. of hot water to extract all soluble material. Next, it is washed on the filter with 150 ml. of cold water. While still somewhat moist it weighs about 1300 g. and is free from both Rb and Cs. [A sample dissolved in dilute HCl and treated with a silicomolybdate solution (see below) forms no precipitate even after standing for several hours.] The combined filtrates are evaporated until crystallization begins. The “second synthetic carnallite” precipitated overnight from the cooled solution amounts to about 2270 g. and contains all the Rb and Cs. The concentration of these elements is thus three times higher than in the first synthetic carnallite. The mother liquor gives no precipitate on addition of a silicomolybdate solution even if allowed to stand for many hours.

The second synthetic carnallite can be further enriched by repetition of the crystallization. However, this is not necessary.

To precipitate the silicomolybdate salts, 2.3 kg. of the second carnallite is dissolved in 2.9 liters of warm water and treated with 0.9 liter of concentrated hydrochloric acid. The KCl (about 70 g., free of Rb and Cs) which separates out on cooling to room temperature is filtered off and the solution is reheated to 60–70°C. Vigorous agitation is then started and the solution is treated with sufficient amount of molybdosilicate solution (see p. 953) to precipitate one-tenth of the total available silicomolybdate Rb₄[SiMo₁₂O₄₀·2H₂O] and Cs₄[SiMo₁₂O₄₀·2H₂O]. The required quantity of solution is determined on a sample. Usually, more reagent will be needed than indicated by stoichiometry. The precipitate starts to form on cooling to 40–50°C and requires 12–15 hours for complete settling.
The clear supernatant liquid is then decanted. The scaly precipitate, which adheres to the walls of the container, detaches after brief drying in air and is quantitatively collected. The precipitate now contains all of the Cs and one tenth of the Rb. The Cs:Rb ratio is now 1:10, instead of the original 1:100. The silicomolybdate precipitate is then worked up to obtain the CsCl. It is placed in a porcelain boat, which is then inserted in a Pyrex tube. If larger quantities are handled, the precipitate may also be placed in a second tube and distributed in a layer not more than 0.5 cm thick. This second tube is then concentrically inserted into the first. The assembly is heated in an electric furnace to 450°C while HCl gas, saturated with CCl₄, in a wash bottle filled with liquid CCl₄, is allowed to flow through the tube. The CCl₄ vapor is thermally decomposed to C₂Cl₆ and Cl₂. The latter is to prevent the formation of a small amount of volatile low-valence Mo compounds. Loose crystalline deposits of Mo(OH)₂Cl₂ are formed in the rear, cold portion of the tube. The exit HCl gas is passed through a water-filled wash bottle to absorb any entrained Mo(OH)₂Cl₂. To remove all traces of Mo from the product mixture of alkali chlorides, Cl₂ is passed through the apparatus for a short time. This is done toward the end of the reaction, which lasts 1.5 hours. During the final stage of conversion the temperature is increased to incipient red heat.

The pure white residue consists of RbCl, KCl, CsCl and SiO₂. It is repeatedly extracted with hot water, and the silicic acid is filtered off. The filtrate is evaporated to dryness. To separate KCl and RbCl from CsCl, 16 g. of dry residue is dissolved in 40 ml. of warm 2.5N HCl and treated with 50 ml. of warm 96% alcohol. After cooling, the first KCl-RbCl precipitate is filtered off and the filtrate is heated and again treated with 300 ml. of warm 96% alcohol. Upon cooling, the second RbCl-KCl precipitate is filtered off and the filtrate once more treated with 50 ml. of alcohol and filtered as above. The filtrate is evaporated; the residue contains all the CsCl. It is dissolved in 20 ml. of 2.5N HCl and treated with 5 ml. of 20% SbCl₃ solution in 7.5N HCl. After a while, the Cs precipitates out as the chloroantimonate. The concentration of RbCl in the entire resulting solution must not exceed 1 M following the addition of the SbCl₃, since otherwise rubidium chloroantimonate is coprecipitated. The cesium chloroantimonate is then placed in a boat and heated in a stream of HCl gas at 250°C. The SbCl₃ distills off and the CsCl remains as a residue. It can be tested spectroscopically for K and Rb.

The mother liquor from the cesium chloroantimonate precipitate still contains a considerable amount of Cs. It is evaporated to dryness and the residue is freed of SbCl₃ by distillation in a stream of HCl. The resulting mixture of CsCl, RbCl and some KCl is added to the material treated with alcohol to separate the RbCl.
To obtain rubidium, the filtrate from the first fractional precipitation of silicomolybdates is used to dissolve the first fraction of the RbCl-KCl precipitate obtained during the separation of CsCl by treatment with alcohol. Next, the silicomolybdate reagent is added until the solution acquires a permanent yellow color, and most of the Rb present completely precipitated. The precipitate is washed four times (vigorous stirring) with 200-ml. portions of 2.5N HCl, filtered through a fritted glass filter, dried in a vacuum desiccator, decomposed in an HCl stream, and is finally freed of SiO₂, as described above.

The dry residue so obtained consists of RbCl-KCl and is combined with the second and third RbCl-KCl fractions previously obtained in the separation of CsCl by alcohol treatment. The combined residue is redissolved in 180 ml. of 2.5N HCl and once more treated with the silicomolybdate reagent. The latter is added in portions with vigorous stirring until complete precipitation results. The precipitate is washed twice (vigorous stirring) with 60-ml. portions of 2.5N HCl, filtered as above and dried. Finally, it is converted to the chloride and freed of SiO₂. The purity of the resulting RbCl can be tested spectroscopically.

If the negligible amount of CsCl carried along with the RbCl is not harmful, the latter can be completely precipitated in a single step.

If larger quantities are desired, the wet method of silicomolybdate decomposition is more convenient. The latter complex is treated with barium hydroxide solution saturated at low temperature. (To avoid working with excessive quantities of liquid, part of the Ba(OH)₂ can be added as the solid.) The amount added must exceed by 20% the amount required to decompose the complex into barium molybdate, barium silicate and RbOH (CsOH). The mixture is then boiled for thirty minutes. Flame gases containing CO₂ should not come in contact with the mixture or large amounts of Ba(OH)₂ will be converted to worthless BaCO₃. The barium molybdate and barium silicate which separate are not filtered off until after the reaction mixture has cooled. The filtrate is then saturated with CO₂ and boiled for fifteen minutes. The BaCO₃ precipitate is filtered off and the filtrate is evaporated with simultaneous addition of hydrochloric acid. The residue contains RbCl and CsCl free of Mo and Ba.

**Preparation of silicomolybdate reagent:** A boiling solution of 60 g. of NaOH in 400 ml. of H₂O is prepared, and 172 g. of MoO₃, free of ammonium salts, is added in small portions over a period of 10-15 minutes. Heating is then stopped and 500 ml. of cold water is poured into the solution. Next, 250 ml. of HNO₃ (d. 1.39) is diluted with water to a volume of 350 ml. and is added. Although the addition should be rapid, only small portions are added at one time. Vigorous agitation must be maintained throughout. No
permanent precipitate should form during these additions. Immedi­ately thereafter, a silicate solution is added in a thin jet and with vigorous stirring. The solution is prepared from 28 g. of Na$_2$SiO$_3$ · 9H$_2$O dissolved in 125 ml. of 2N NaOH and boiled for 10-15 min.

The deep-yellow silicomolybdate solution is concentrated on a water bath to a volume of 700-800 ml. At this point some ammonium silicomolybdate may separate out if the MoO$_3$ used was not completely free of the NH$_4$ salt.

Recovery of molybdosilicate solution. The silicate-containing precipitate of barium molybdate is boiled for 30 minutes with a slight excess of sodium carbonate solution, using vigorous stir­ring. On cooling, the silicate and carbonate are filtered off. A silicomolybdate solution is then prepared from the filtrate, which contains all of the molybdic acid in the form of Na molybdate. The directions are the same as given above. The only difference is that 280 ml. of concentrated nitric acid is required here, instead of 250 ml., because the Na molybdate solution still contains a slight excess of Na$_2$CO$_3$ (caution: violent foaming occurs on addi­tion).

The excess of silicomolybdate reagent, which is added to the HCl solution of carnallite in order to completely precipitate the Rb, can be separated off as yellow ammonium silicomolybdate upon addition of an excess of a concentrated aqueous solution of NH$_4$NO$_3$. Molybdic acid is recovered from the above ammonium salt by the same method as used for processing Rb silicomolyb­date.

II. Other methods. The industrial D'Ans process uses tetra­oxalates in the preparation of Rb (and Cs) from carnallites. In this method rubidium carnallite, previously isolated by a series of fractional precipitations, is dissolved in a small amount of water and the hot solution treated with an excess of oxalic acid. This excess should be so large that after cooling and separation of RbH$_3$(C$_2$O$_4$)$_2$ · 2H$_2$O the strongly acid solution (HCl) will still be saturated with oxalic acid. This can be easily checked under a microscope. The well-crystallized tetraoxalate is suction fil­tered and recrystallized from hot water. The tetraoxalates of Rb and Cs are similar, both being readily soluble in hot water. If it is desired to obtain the Cs, which is present together with the Rb, a brief series of fractional precipitations of the oxalate must be performed. As a result, the Cs, which is the more soluble com­ponent, will concentrate in the mother liquor. The Rb tetraoxalate is converted to carbonate by calcination at a moderate tempera­ture, immediately yielding a pure-white product free of traces of Cs.

The precipitation of Rb and Cs in the laboratory is not quite complete. Even though the mother liquor, containing hydrochloric
and oxalic acid, can be further processed to obtain the residual amounts of Rb and Cs \([\text{together with } \text{Mg(OH)}_2]\), this can be done effectively only on an industrial scale.

**PROPERTIES:**

RbCl: Formula weight 120.9. M.p. 717°C, b.p. 1383°C. Solubility (0.55°C) 77.34; (18.70°C) 90.32; (114.0°C) (b.p.) 146.65 g. RbCl/100 g. H₂O. Solubility in ethyl alcohol (25°C): 0.078 g. RbCl/100 g. alcohol. d. (x-ray) 2.79. B₁ structure type.

CsCl: Formula weight 168.4. M.p. 645°C, b.p. 1303°C. Solubility (0.70°C) 162.29; (16.20°C) 182.24; (119.4°C) (b.p.) 289.98 g. CsCl/100 g. H₂O. d. (x-ray) 3.99. B₂ structure type.

**REFERENCES:**

G. Jander and F. Busch, Z. anorg. allg. Chem. 187, 165 (1930);
194, 38 (1930).


**CESIUM CHLORIDE AND CESIUM ALUM FROM POLLUCITE**

**CESIUM CHLORIDE**

Pollucite (pollux) is a cesium aluminum silicate, about one-third of which is Cs₂O. Lenher, Kemmerer and Whitford recommend the following method for obtaining Cs from this mineral.

The mineral is thoroughly pulverized and about 5 kg. of it is passed through a fine-mesh flour sieve. Such fine division of the mineral ensures slow but complete decomposition with concentrated hydrochloric acid. After evaporating the hydrochloric acid and dehydrating the silicic acid at 110°C, the mass is extracted with 3N HCl (this is the optimal concentration for subsequent precipitation of Cs–Sb chloride) and the Cs is precipitated as cesium antimony chloride, 3CsCl · 2SbCl₃, on adding a slight excess of a solution of SbCl₃ in 3N HCl. A small amount of CsCl remaining in solution can be recovered by evaporating the filtrate, dissolving the residue in 3N HCl, and precipitating with the SbCl₃ solution.

The cesium antimony chloride is hydrolyzed by boiling with water. The solution contains the Cs, a very small amount of Sb, and traces of Fe and Al. The Sb is precipitated with H₂S; the CsCl is either obtained directly by evaporating the solution, or else it is converted first to nitrate and then to carbonate (see "Very Pure Alkali Metal Carbonates"). The yield is about 37%, based on the original pollucite.
CESIUM ALUM

The alkali metals and Al are present in pollucite in about the right proportions for the formation of alum. Hence, the procedure of Clusius and Stern can be followed. The mineral is decomposed with hydrochloric acid and Cs is precipitated as a low-solubility alum by treatment with sulfuric acid. Thus, for example, 0.5 kg. of very finely pulverized (0.01 mm.) pollucite in one liter of 18% hydrochloric acid is evaporated to dryness on a water bath. This procedure is repeated three times, and each time the dry residue is extracted with one liter of H$_2$O + 100 ml. of concentrated hydrochloric acid. This is followed by suction filtration on a filter cloth. The filtered extracts are combined and concentrated to one liter, and the silicic acid, which separates out almost completely, is decanted. The alum is then gradually precipitated with 200 ml. of concentrated H$_2$SO$_4$. After cooling, about 545 g. of crude yellowish alum is obtained. The mother liquor is practically free of Cs. The crystallization is repeated several times, in each case dissolving 250 g. of the alum in 2.5 liters of boiling water in a four-liter Erlenmeyer flask. On slow cooling (constant agitation, 10 hours) the alum again separates out. The material obtained after six crystallizations shows no traces of other alkali metals. One way to ensure pure alum is to check the purity of the mother liquor from which it is precipitated. The specific conductivity of a pure Cs alum solution is $1.39 \times 10^{-3} \ \Omega^{-1} \cdot \text{cm.}^{-1}$ (measured at 25°C, saturated solution).

REFERENCES:

V. Lenher, G. Kemmerer and E. Whitford, Ind. Eng. Chem. 16, 1280 (1924).

FREE ALKALI METALS

ELECTROLYTIC PREPARATION OF LITHIUM

\[
\text{LiBr} = \text{Li} + \frac{1}{2} \text{Br}_2
\]

Pure Li is prepared (via the method of Ruff and Johannsen) from LiBr which is melted in an electric arc in the presence of 10-15% LiCl (the LiBr is obtained from Li$_2$CO$_3$ by evaporating the latter from hydrobromic acid). Fig. 260 is a scale drawing (1:5) of the Muthmann electrolysis vessel used for the melting procedure. It is made of copper and its upper part is cooled with water. While
the melting point of pure LiBr is about 546°C and that of LiCl is 606°C, a mixture of LiBr with 13% LiCl solidifies at 520°C. The electrolysis proceeds at 10 v. (as measured across the terminals) and 100 amp. A graphite rod is used as an anode and two 4-mm. iron wires serve as cathodes. The metal, which deposits at the cathodes, is scooped up from time to time with a flat iron spoon and, while still liquid, is separated from the solidified melt on a cold stone plate. It is next freed of adhering salt using Borchers' method, i.e., by immersion in a paraffin bath (180-200°C). The salt settles to the bottom, while the metal rises to the surface. After cooling, it is washed with ligroin. It is stored under ligroin (d. 0.56) in completely filled, tightly closed vessels.

REFERENCES:
O. Ruff and O. Johannsen, Z. Elektrochem. 12, 186 (1906).
W. Borchers, ibid. 3, 39 (1895).

PURIFICATION OF TECHNICAL GRADE LITHIUM:
REMOVAL OF POTASSIUM

Technical grade lithium prepared by electrolysis of a fused, low-melting mixture of LiCl and KCl is, according to Ruff and Johannsen, contaminated with a few percent of potassium. The latter is removed by the Guntz and Broniewski procedure. The Li is converted to LiH by heating in a stream of H₂ at 700-800°C (see the preparation of LiH). The potassium volatilizes in the metallic form, since its hydride is unstable at this high temperature. The LiH is then decomposed under vacuum at 1000°C, the purified Li being condensed on a water-cooled iron cylinder mounted in the reaction vessel.

REFERENCES:
O. Ruff and O. Johannsen, Z. Elektrochem. 12, 186 (1906).

ALKALI METALS OBTAINED BY REDUCTION WITH ZIRCONIUM

Dissolved gases trapped during preparation are particularly difficult to remove from alkali metals. The removal of these gases
requires repeated distillation under vacuum, and even then the complete separation is difficult to achieve. Therefore, laboratory methods for preparation of pure alkali metals should avoid any contact of gases with the nascent metal. According to De Boer, and also Broos and Emmens, the reduction of alkali chromates as well as of bichromates, molybdates and tungstates with zirconium powder meets the above specification, particularly well.

\[
2\text{Cs}_2\text{CrO}_4 (\text{Rb}_2\text{CrO}_4, \text{K}_2\text{CrO}_4, \text{Li}_2\text{CrO}_4) + \text{Zr} = 4\text{Cs} (\text{Rb}, \text{K}, \text{Li}) + \text{Zr(CrO)}_2
\]

\[
\begin{array}{c|c|c|c|c|c}
& 763.7 & (573.9; 388.4; 259.8) & 91.2 & 531.6 (341.9; 156.4; 27.8) & 323.2 \\
\text{Heating temperature} & 725^\circ\text{C} (700^\circ\text{C} \text{or} 800^\circ\text{C}) \\
\text{Yield} & 90-96\% & \text{Rb} \text{practically quantitative} & \text{K up to} 80\% \\
\end{array}
\]

To prepare pure Cs, Rb or K, one part by weight of Cs$_2$CrO$_4$ (Rb$_2$CrO$_4$ or K$_2$CrO$_4$) is mixed with four parts by weight of fine Zr powder. The mixture is compressed into rods and heated in a highly evacuated, thoroughly preheated quartz tube (or other suitable apparatus).

The reactions start smoothly at 725$^\circ$C (700 or 800$^\circ$C). The heating is continued until a temperature of 1000$^\circ$C is reached. The alkali metals form oxide-free shiny, mirrorlike deposits on the colder parts of the tube. Yields: Cs 90-96%; Rb practically quantitative; K up to 80%.

To prepare Li it is necessary to mix Li$_2$CrO$_4$ with eight parts by weight of Zr to prevent explosive reduction between 450 and 600$^\circ$C. The yield of the metal is very low.

In cases where, for reasons associated with the limitations of equipment, the temperatures required for the preparation of pure Cs, Rb and K from chromates cannot be used, bichromate mixtures consisting of one part of Cs$_2$Cr$_2$O$_7$ (Rb$_2$Cr$_2$O$_7$, K$_2$Cr$_2$O$_7$) to ten parts of Zr must be used. A smooth reduction will start at about 380$^\circ$C (370$^\circ$, 380$^\circ$C). The yield of Rb is 80-90%. It is free of oxide, as is the potassium formed in this reaction. The Cs product, however, contains some oxide, but, if the mixture ratio is changed to one part of Cs$_2$Cr$_2$O$_7$ to 20 parts of Zr, the Cs will be free of oxide.

To prepare pure Na it is best to replace the deliquescent chromate or bichromate by Na$_2$MoO$_4$ or Na$_2$WO$_4$, which is mixed with four parts by weight of Zr powder. Evolution of sodium vapor begins smoothly at about 550$^\circ$ or 450$^\circ$C, respectively. With Na$_2$MoO$_4$ the yield is practically quantitative, and with Na$_2$WO$_4$ it is 80%. The Na is free of oxide. For the preparation of Rb and Cs chromates or bichromates, see the section on chromium.
According to the following equations, Li₂CrO₄ is formed on boiling a solution of (NH₄)₂Cr₂O₇ with LiOH; Na₂MoO₄ and Na₂WO₄ are obtained by the reaction Na₂CO₃ with MoO₃, or WO₃ respectively.

\[
4 \text{LiOH} + (\text{NH}_4)_2\text{Cr}_2\text{O}_7 = 2\text{Li}_2\text{CrO}_4 + 2\text{NH}_3 + 3\text{H}_2\text{O}
\]

\[
\text{Na}_2\text{CO}_3 + \text{MoO}_3(\text{WO}_3) = \text{Na}_2\text{MoO}_4(\text{Na}_2\text{WO}_4) + \text{CO}_2
\]

REFERENCES:


ALKALI METALS OBTAINED BY DECOMPOSITION OF AZIDES

Suhrmann and Clusius succeeded in preparing very pure, gas-free alkali metals by thorough decomposition of their azides under high vacuum.

\[
\text{NaN}_3 (\text{KN}_3; \text{RbN}_3; \text{CsN}_3) = \text{Na} (\text{K}; \text{Rb}; \text{Cs}) + \frac{3}{2}\text{N}_2
\]

The equipment used (Fig. 261) must be Pyrex which is not seriously attacked by Na, K, Rb, Cs or Li.

When "physically pure" alkali metals are to be prepared, all the glass parts of the equipment are joined by fusion and there

![Fig. 261. Preparation of alkali metals from azides. r) Decomposition tube; v₁, v₂) receivers; a) ampoule for storing the metal; b, c) fused joints; k₁, k₂) cooling traps; q) mercury valve.](image_url)
are no greased stopcocks in that part of the apparatus which is under vacuum. In other cases, where purity requirements are less vigorous, the use of ground joints and stopcocks is permissible. These, however, must not come in contact with the liquid alkali metal or its vapor.

The azides are finely pulverized in an agate mortar and placed in a retort \( r \) (amounts: 10-12 g. of NaN\(_3\) or KN\(_3\), 6-7 g. of RbN\(_3\) or CsN\(_3\)). The salt, which fills about one quarter of the retort, is then distributed over the entire tube. However, RbN\(_3\) and CsN\(_3\) are not placed directly in the retort. Instead, a quartz tube sealed at one end is filled with the salt and inserted into the retort. Next, \( r \) is sealed onto the rest of the apparatus and the latter is evacuated by means of a high-speed forepump. (In the original preparation, a mercury diffusion pump made of glass was used.) At the same time the apparatus is thoroughly heated to remove traces of gases. The cooling tubes \( k_1 \) and \( k_2 \) are kept immersed in liquid nitrogen until the end of the experiment. An electric heater is pushed over \( r \) and a temperature of 200°C is maintained for 12 hours, while the apparatus is continuously evacuated. A Geissler tube, connected to the apparatus as a vacuum gauge, must always show a high vacuum (ready discharge). Next, the furnace temperature is gradually raised and the mercury valve \( q \) is closed, to avoid entrainment of the azide by the free N\(_3\) during the subsequent decomposition and its deposition in receiver \( v_2 \). The decomposition temperatures of the azides are: NaN\(_3\), 275°C; KN\(_3\), 355°C; RbN\(_3\), 395°C (quartz tube); CsN\(_3\), 390°C (quartz tube). Decomposition of NaN\(_3\) begins before the melting point is reached; KN\(_3\) melts at 343°C, RbN\(_3\) at 321°C, CsN\(_3\) at 326°C. At the start of the decomposition, the temperature is adjusted in such a way that pressure in the apparatus is not above 0.1 mm. To prevent a sudden pressure rise, a surge vessel is connected to the apparatus via a stopcock. This is an eight-liter vessel, thoroughly evacuated by means of the forepump. To assure rapid pressure relief all tubing must be 12 to 16 mm. in diameter. The decomposition sometimes does not start until 3-4 hours after the proper temperature is reached (especially in the case of KN\(_3\)). The azides, should not be overheated because an explosive decomposition may occur and the apparatus destroyed.

The end of the decomposition is indicated by cessation of discharge of the Geissler tube (high vacuum). As the N\(_3\) pressure decreases, the alkali metal formed is distilled from \( r \) into collector \( v_1 \). The retort \( r \) is then sealed off at point \( b \) and the stopcock to the surge vessel is closed, while the forepump is still operating. The high-vacuum pump (in the original, a mercury diffusion pump made of glass) is then started and the mercury valve \( q \) is opened. Then the connection to the forepump is sealed off at \( c \). The pressure in the apparatus is reduced to below 10\(^{-7}\) mm. Under these
18. ALKALI METALS

In more successful work the decomposition is completed in 3 to 4 days as described provided the pressure is not allowed to rise above 0.1 mm.; in less successful preparations it takes 6 to 8 days. The alkali metals thus obtained are completely free of gas, so that no pressure rise is observed on heating them under high vacuum.

The yield of these alkali metals is approximately 100% for NaN₃, 80% for KN₃, 60% for RbN₃, and 90% for CsN₃. The residue is light brown in the case of KN₃, blue-green in the case of RbN₃, and yellowish-gray in the case of CsN₃. It consists of the nitride mixed with silicate and undecomposed azide.

REFERENCES:

RUBIDIUM AND CESIUM OBTAINED FROM THE CHLORIDES

\[
\text{RbCl (CsCl)} + \frac{1}{2} \text{Ca} = \frac{1}{2} \text{CaCl}_2 + \text{Rb (Cs)}
\]

120.9 (168.4) 20.0 55.5 85.5 (132.9)

This method, proposed by Hackpil, 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 is filled with the mixture and stoppered with a plug 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.](image-url)
After reaction vessel α 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 ο 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 α 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 t 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 N₂ 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.

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%.

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

REFERENCES:

G. Brauer, private communication.

PROPERTIES OF ALKALI METALS

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>6.940</td>
<td>179.0</td>
<td>1336</td>
<td>0.534</td>
</tr>
<tr>
<td>Na</td>
<td>22.997</td>
<td>97.8</td>
<td>883</td>
<td>0.97</td>
</tr>
<tr>
<td>K</td>
<td>39.006</td>
<td>63.5</td>
<td>762</td>
<td>0.86</td>
</tr>
<tr>
<td>Rb</td>
<td>85.48</td>
<td>39.0</td>
<td>696</td>
<td>1.52</td>
</tr>
<tr>
<td>Cs</td>
<td>132.91</td>
<td>28.6</td>
<td>670</td>
<td>1.89</td>
</tr>
</tbody>
</table>

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 H₂. (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 Løgstrup, 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 point $A$ and evacuated by means of a mercury diffusion pump connected 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 containing 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 $E$, 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:

P. Ehrlich, see the section on Alkaline Earth Metals, Ca.
D. Lely, Jr., and L. Hamburger, Z. anorg. Chem. 87, 209 (1914).

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 CO₂ 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$_2$O, 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.

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 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.

Fig. 265. Filling of glass spheres with oxide-free alkali metal.
down to level $s$, thus forming a discontinuity. The metal will be retained in the sphere only if the latter has been thoroughly pre-dried 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:


SODIUM DISPERSIONS IN INERT LIQUIDS

Dispersions of molten Na (d. at 100°C, 0.928) in inert liquids containing about 50% metallic Na (particle size 1-20 millimicrons) can be prepared in the laboratory by mechanical dispersion. The boiling point of the inert liquid must be higher than the melting point of Na (97.5°C). Such liquids include toluene, xylene, some light mineral spirits, kerosene, heptane, n-octane, mineral oil, and naphthalene. Appropriate agents (0.25-1%) contribute to the reduction of particle size (soot, copper powder, pyridine, etc.) or stabilize the dispersion (oleic acid, aluminum stearate, calcium stearate, etc.).

The usual safety devices generally employed in working with Na and with flammable solvents (such as goggles, safety shields, gloves, purged and sealed heaters, etc.) must be used in the preparation of $N_2$ dispersions. In case of fire, the burning Na should be covered with dry soda. Carbon tetrachloride extinguishers should not be used. Carbon dioxide extinguishers may be used in fighting solvent fires.

Disk-shaped stirrers with beveled teeth* (see Fig. 266c) as well as turbine-type agitators** which entrain the liquid along the

---

*Manufactured by Cowles Dissolver Co., Cayuga, N.Y., and others.

**Manufactured by Premier Mill Corp., Geneva, N.Y., and others.
axis and eject it centrifugally through narrow slots (Fig. 266) are
effective devices for dispersing Na.

The U.S. Industrial Chemicals Co. has suggested using a two-
liter vessel, (diameter about 15 cm.) with a disk stirrer about 7.5
cm. in diameter, rotating at 4000–6000 r.p.m. (see Fig. 266). With
an agitator diameter of 2.5 cm. and a speed of 8000–15,000 r.p.m.,
a half- to three-liter flask is recommended.

![Vessel and stirrers for Na dispersion in inert liquids.](image)

A cleaned and dried apparatus is charged with 400 g. of dry
dispersing medium and the substance selected as a dispersion aid
is added to the latter with slow stirring. The air is displaced with
nitrogen, the stirring is stopped, and 400 g. of bright Na shavings
is introduced into the apparatus. The apparatus is then again
flushed with N₂. All of the Na melts on heating to 105°C, and the
stirrer is restarted and brought slowly to top speed.

As the particle size decreases, the mixture turns a deeper
shade of gray. In most cases, the particle size drops to 10–15
microns within 10–15 min. If the particles still appear too large
when examined under a microscope, the stirring is continued for
another five minutes. The dispersion is then left to cool to or
below 80°C without any stirring. The stirring can be resumed
below 80°C since the particles will not recoalesce. When the dis-
persion is at room temperature it may be poured into dry storage
vessels.
Sodium dispersions should be stored in tightly closed vessels under a nitrogen blanket. Air or moisture destroy the dispersion and may easily cause a fire. For safety the glass storage vessels should be placed inside a protective vessel and embedded in diatomaceous earth. Iron vessels are also worth considering as storage containers. Storage vessels must be free of Na traces both on the outside and in the area of the stopper. Filter paper used to remove the sodium remnants must be well impregnated with kerosene. Dry paper, linen and the like ignite as soon as they come in contact with Na dispersions.

Where less concentrated dispersions are used, it is best to dilute the stock just before use. The dilution fluid should have a boiling point below the melting point of Na.

After emptying the apparatus the reactor is first rinsed with kerosene and then treated with water vapor (which must be free of liquid water) to react the last traces of Na.

REFERENCES:


FINELY SUBDIVIDED SODIUM ADSORBED ON INERT SOLIDS

Molten Na spreads spontaneously on the surface of inert solids at 100 to 200°C in a N₂ atmosphere; monatomic sodium layers can thus be achieved. Suitable solid substances are NaCl, Na₂CO₃, carbon (charcoal), metal powders, Al₂O₃ and SiC. In some cases the reaction products prepared with the aid of finely subdivided metallic Na themselves prove to be effective carriers. Carrier materials consisting of fine particles coated with metallic Na remain free flowing over a wide range of temperatures and concentrations. Depending on its grain size, common salt will adsorb 2-10% Na. Soda adsorbs 10% Na, aluminum oxide 20-25%, activated carbon 30%. These substances remain free flowing up to the melting point of Na. At high Na contents, the materials convert to pastes.

The table below gives the optimum dispersing temperatures, the contents of finely subdivided Na and the appearance of the mixtures with some carrier materials.

According to a laboratory manual published by the National Distillers Chemical Co. a well-dried three-necked Pyrex flask, capacity 1-3 liters, may be used as the reactor (see Fig. 267). A stirrer with a graphite-packed gland is inserted through the middle neck. The other two necks serve for filling and temperature measurement.
Optimal dispersing Sodium

<table>
<thead>
<tr>
<th>Carrier material</th>
<th>Optimal dispersing temperature, C</th>
<th>Sodium content, %</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated alumina</td>
<td>140-160</td>
<td>20-25</td>
<td>black</td>
</tr>
<tr>
<td>Activated coconut charcoal</td>
<td>120</td>
<td>&gt;35</td>
<td>silver to black</td>
</tr>
<tr>
<td>Iron powder (150μ)</td>
<td>150-200</td>
<td>5</td>
<td>gray (pyrophoric)</td>
</tr>
<tr>
<td>Colloidal carbon</td>
<td>170</td>
<td>&gt;30</td>
<td>black (pyrophoric)</td>
</tr>
<tr>
<td>Common salt (180-420μ)</td>
<td>150</td>
<td>2-10</td>
<td>gray to black</td>
</tr>
<tr>
<td>White sand (420-840μ)</td>
<td>150-165</td>
<td>5</td>
<td>gray</td>
</tr>
<tr>
<td>Calc. soda (50-150μ)</td>
<td>150</td>
<td>10</td>
<td>gray to black</td>
</tr>
<tr>
<td>Zirconium oxide (50μ)</td>
<td>250</td>
<td>10</td>
<td>dark gray</td>
</tr>
</tbody>
</table>

A tube on each neck serves as the inlet and outlet for the nitrogen. The flask is heated by means of a tightly fitting electrical heating mantle. A dish is placed below the apparatus as a safety pan in case of breakage. An oil bath may also be used for heating. The same safety measures as those mentioned in the preceding section must be observed.

The flask is charged with, for example, 300 g. of dried, calcined sodium carbonate and the air is displaced with dry N₂. By stirring at 100-300 r.p.m., the soda is whipped to about twice the original volume, while it is heated to 150°C. Then 10 g. of Na (in pieces weighing 2-5 g.) is added through the filling neck. As soon as the Na melts the stirring is accelerated and the high speed is maintained for about five minutes. As the Na distributes over soda, the latter changes from white to gray.

Wherever possible, finely subdivided Na is used directly following its preparation, and the reaction for which it is intended is carried out in the same vessel in which the Na dispersion has been prepared. If, however, the dispersion must be stored in another container for future use, the transfer should be done under N₂ after precooling of the apparatus in a nitrogen stream. Well-dried metal storage containers should be used for this purpose. They must be kept in a dry place and away from flammable materials.

To decompose Na finely dispersed on solid materials, it is burned in some safe spot, inside an open iron vessel. If necessary, a little kerosene may be added beforehand to produce complete combustion. Small residues of fine Na remaining in the reaction vessel are reacted with dry steam (or rapid stream—use a protective shield) in the reactor previously flushed and filled with N₂.
REFERENCES:

High Surface Sodium, National Distillers Chemical Co., Ashtabula (Ohio) 1953.

Alkali Hydrides

NaH, KH, RbH, CsH and LiH

\[
\text{Li (Na, K, Rb, Cs) + } \frac{1}{2} \text{H}_2 = \text{LiH (NaH, KH, RbH, CsH)}
\]

6.9 (23.0; 39.1; 85.5; 132.9) 7.95 (24.0; 40.1; 86.5; 133.9)

NaH, KH, RbH, CsH

The hydrogenation apparatus shown in Fig. 268 is designed to prepare NaH, KH, RbH and CsH following the procedure of Zintl and Harder. A seamless steel liner tube \( \alpha \) is inserted into a quartz or Vycor tube \( \gamma \) as protection against corrosion by alkali metal vapors. Liner \( \alpha \) is preheated for many hours in moist H\(_2\) at 900°C to decarbonize the steel. As iron boat \( \beta \) is placed in sheet iron cylinder \( \delta \), which is closed on one side. After prolonged evacuation of the apparatus the surfaces of \( \alpha, \beta \) and \( \omega \) are deoxidized by passage of electrolytic H\(_2\) (inlet at \( \lambda \) and outlet at the loosely fitting joint \( \iota \)) and simultaneous prolonged heating of \( \alpha, \beta \) and \( \omega \) to dull red heat, using an electric oven.

The electrolytic H\(_2\) must be very thoroughly freed of O\(_2\) and H\(_2\)O and before entering the reaction zone must pass through a large U tube filled with resublimed P\(_2\)O\(_5\).

Sodium (or potassium) must be freed from adhering high-boiling hydrocarbons prior to use. To this end, they are remelted repeatedly under xylene and, when as oxide-free as possible, are placed in boat \( \psi \).

Rubidium and cesium can be prepared in the reactor itself (see section on Alkali Metals Obtained by Reduction with Zirconium, p. 957). In this procedure, the boat is charged with a mixture of Rb\(_2\)CO\(_3\) or Cs\(_2\)CO\(_3\) and magnesium powder, using a mole ratio of 1:3 (weight ratios are 231.0:73.0 or 325.8:73.0, respectively). The mixture is predried under vacuum at 150°C. The apparatus is evacuated and cylinder \( \delta \) with boat \( \omega \) are slowly heated. In the case of Na and K, the temperature is raised to 300–350°C (at which temperature the metals distill). In the case of Rb and Cs, the temperature is 620°C. The alkali metals condense inside the steel liner at \( \alpha \). After cooling, tube \( \delta \) with boat \( \omega \) containing impurities and/or residues are pulled out from the reaction zone (still under a H\(_2\) stream) through ground glass joints \( \iota \). With manometric valve \( \nu \) reconnected, the air is displaced with
H₂ and the alkali metal is slowly evaporated by heating at 300–400°C and 1 atm. in a stationary hydrogen atmosphere. The hydride formed under these conditions is deposited on both sides outside the heated zone, mostly in the form of cottonlike clusters of colorless, crystalline needles. If the evaporation of the metal is too rapid, the hydride becomes contaminated with condensed metal. From time to time the tube is refilled with H₂ to keep the pressure at 1 atm. When the manometric valve \( \nu \) shows no further pressure drop over a period of 24 hours, the hydride is removed (under a hydrogen stream) from \( \alpha \) by pushing it into tube \( \delta \) with a small Pt scoop sealed onto a long glass rod and introduced through \( s_1 \). Tube \( r \) is then removed and \( s_3 \) is closed off. The hydride can then be transferred to other containers by opening \( s_4 \), under a stream of H₂.

![Fig. 268. Preparation of alkali metal hydrides; \( r \) quartz or Vycor reaction tube; \( \alpha \) protective iron liner; \( b \) boat-shielding iron cylinder; \( c \) iron boat.](image)

A finely subdivided NaH suspension may be prepared following a procedure suggested by Ziegler, Gellert, Martin, Nagel and Schneider.

Metallic Na and a dispersing medium are heated at 200–220°C with brisk stirring, using an autoclave provided with a magnetic stirrer (rotary and rocking autoclaves are less suitable). At the same time, electrolytic H₂ is forced in from a steel cylinder or with a compressor. Hydrogenation takes place at all pressures. The higher pressure level is important only insofar as it determines the rate of H₂ uptake.

For each liter of reaction volume, 500 ml. of dispersing agent and 75 g. of Na are used. Suitable dispersing media include hexane, heptane, octane (alone or in mixtures), cyclohexane, methylcyclohexane and ethylcyclohexane. It is best to use a dispersing medium with a critical temperature above 200°C. Aromatic media cannot be used since NaH is a very active hydrogenation catalyst.
at high temperatures, and thus \( \text{H}_2 \) would be lost through hydrogenation of the dispersing medium.

When the \( \text{H}_2 \) uptake ceases, the coarse-grained suspension of NaH may be removed from the autoclave. If the suspension is then ground in a ball mill, its color changes sharply from white to gray-black. The reason for this is that the residual metallic Na in the product becomes finely subdivided. In such cases, the hydrogenation must be repeated, as above. The final pure white suspension will retain its color even after wet grinding. If, following the first hydrogenation, the heating is continued for 2-3 hours at 280-300°C under compressed \( \text{H}_2 \), the suspension will remain white even upon first wet grinding. Repeated hydrogenation for such material is superfluous.

LiH

Zintl and Harder prepared LiH in a boat made of electrolytic iron and charged with shiny Li under Ar. Since molten Li diffuses through iron, a second electrolytic iron liner is inserted into steel tube \( \alpha \). The hydrogenation proceeds rapidly at 600°C and is complete at 700°C. At this temperature, the LiH product is liquid (m.p. 680°C). On cooling, it becomes coarsely crystalline and appears completely colorless and transparent. The boat is pushed into tube \( \beta \) with a long rod (see above) and ground joint \( s_1 \) is shut. A rotary steel milling cutter, about 5 mm. in diameter (see section on Intermetallic Compounds), is then inserted at \( s_5 \) in order to pulverize the hydride. A bulge in the lower half of tube \( \beta \) provides the necessary support for the boat during this operation.

Following the Albert and Mahé procedure, LiH is prepared in quantities of 1 kg. in a low-carbon steel pot, externally protected from scaling with an aluminized steel jacket. The upper part of the pot and its flat, rubber-gasketed lid are water cooled. The lid has nozzles for \( \text{H}_2 \) input, a vacuum connection, and a thermocouple. Two concentric cylindrical “Armco” iron crucibles are placed inside the pot. These fit snugly inside each other and in the pot.

For 1 kg. of LiH (about 890 g. of Li) the innermost crucible should measure 125 mm. in diameter, 350 mm. in height and have walls 2 mm. thick.

The Li is introduced, and the apparatus is evacuated, filled with \( \text{H}_2 \) and heated. Hydrogen uptake starts at 500°C and becomes vigorous at 650°C. A steady pressure of 0.25 atm. gauge is maintained; heating above 700°C must be avoided. The reaction time is about three hours. After the complete cooling, the LiH is taken out under a blanket of \( \text{CO}_2 \) to prevent spontaneous ignition of readily oxidizable sublimates which deposit on the cold parts of the apparatus.
The entire operation lasts about eight hours and yields well-crystallized, hard LiH about 99.6% pure. It is bluish in spots due to contamination with a slight excess of Li.

PROPERTIES:

Colorless substances, decomposed by moisture. Stability to $O_2$ decreases sharply from LiH to CsH: LiH reacts only at red heat; NaH ignites in $O_2$ at about 230°C; KH, RbH and CsH react at room temperature. Equilibrium hydrogen pressure for LiH is 0.023 mm. at 23.5°C and 70 mm. at 640°C (m.p. 680°C). Vacuum sublimation at 220°C results in partial decomposition. Equilibrium $H_2$ pressure for NaH is 8.0 mm. at 300°C; for KH, 7.3 mm. at 300°C; for RbH, about 100 mm. at 370°C; for CsH, 0.3 mm. at 200°C and 27.8 mm. at 300°C. d. (x-ray) for LiH to CsH: 0.77; 1.36; 1.43; 2.59; 3.41. Crystal structure B1 type.

REFERENCES:

E. Zintl and A. Harder, Z. phys. Chem. (B) 14, 265 (1931); see E. Zintl, A. Harder and S. Neumayr, Z. phys. Chem. (A) 154, 92 (1931).

Alkali Metal Oxides

Li$_2$O, Na$_2$O, K$_2$O, Rb$_2$O, Cs$_2$O

LITHIUM OXIDE

\[
Li_2CO_3 = Li_2O + CO_2
\]

73.9 29.9 44.0

Zintl, Harder and Dauth prepared Li$_2$O by thermal decomposition of pure Li$_2$CO$_3$. Pure lithium carbonate (for purification see p. 987) is decomposed in a Pt boat set inside a porcelain tube which is connected to a mercury diffusion pump. Gas evolution ceases after heating for 50 hours at 700°C, as indicated by a McLeod gauge. The boat then contains pure white oxide, the composition of which can be checked by titration of samples.
For preparation of Li₂O from Li₂O₂, see under Li₂O₂ (p. 979).

PROPERTIES:

More stable than the other alkali oxides; begins to sublime below 1000°C. M.p. above 1625°C. Reaction with water less vigorous. d. (x-ray) 2.00. Cl structure type, (Fluorite).

REFERENCES:


SODIUM OXIDE

I. \[5 \text{NaNO}_3 + \text{NaNO}_3 = 3 \text{Na}_2\text{O} + 8 \text{N}_2\]

Direct oxidation of Na cannot be used to prepare pure Na₂O, since the simultaneously formed peroxide is reduced only with great difficulty to Na₂O by the excess Na. Zintl and Von Baumbach give the following directions for the preparation of pure Na₂O.

A nickel boat \(s\) (Fig. 269), lined with pure sodium azide, is charged with a finely powdered mixture of NaNO₃ (purified by recrystallization and dried at 200°C) and about 5.5 times (by weight) as much NaN₃. The boat is placed in a Pyrex tube \(a\) and slowly heated by means of an electric furnace to 200°C in vacuum (Hg diffusion pump). When the reagents have thus been freed of moisture, the temperature is slowly raised to 270–290°C. (An explosion may occur on too rapid heating). The azide decomposes, imparting a dark gray color to the salt mixture. The stopcock

Fig. 269. Preparation of sodium oxide; \(a)\) Pyrex tube; \(r)\) nickel tube; \(s)\) nickel boat.
leading to the pump is occasionally closed so that the course of the reaction can be followed by means of manometer \( m \). The brown color (nitride formation) disappears with rising temperature. When \( \text{N}_2 \) evolution decreases, the temperature is raised to 350°C. Finally, the excess Na is distilled off in vacuum at 350–400°C. The Ni tube \( r \) protects the Pyrex from corrosion by Na vapor. Before cooling, the Na mirror is removed from the lower half of tube \( b \) by heating with a flame. Thus, no sodium should adhere to the boat as it is withdrawn from the tube. While the Na is being removed from the tube, the furnace must be left on to prevent Na condensation on top of the \( \text{Na}_2\text{O} \) in the boat. The boat containing the preparation is then pulled out through ground joint \( c \), making sure that air is completely excluded. It takes 3 to 5 hours to prepare 0.3–0.5 g. of \( \text{Na}_2\text{O} \). The yield is quantitative, based on \( \text{NaNO}_3 \).

II. \[ \text{NaOH} + \text{Na} = \text{Na}_2\text{O} + \frac{1}{2}\text{H}_2 \]

40.0 23.0 62.0 1.0

This method, according to Klemenc, Ofner and Wirth, enables the preparation of up to 8 g. of \( \text{Na}_2\text{O} \) in a single batch. A nickel crucible is placed in a Pyrex tube, closed off at the bottom and connected at the top to a vacuum line and a long-stem manometer. A mixture of NaOH granules and small Na pieces is used. Because NaOH generally contains a few percent of water, a correspondingly larger quantity of Na must be weighed out. Reaction begins at 300–320°C and the \( \text{H}_2 \) formed is continuously pumped out, maintaining the pressure at 30–40 mm. Finally, the slight excess of Na is distilled off under high vacuum. The product should be pure white. Its average composition is 96% \( \text{Na}_2\text{O} \), 2% \( \text{NaOH} \), 2% \( \text{Na}_2\text{CO}_3 \). It is best stored under anhydrous benzene.

PROPERTIES:

Fine, white powder. d. (x-ray) 2.39. \( \text{CaF}_2 \) lattice (C1). For corrosion resistance of various crucible materials to molten \( \text{Na}_2\text{O} \) and \( \text{Na}_2\text{O}_3 \), see E. G. Bunzel and E. J. Kohlmeyer, Z. anorg. Chem. 54, 4 (1947). According to this reference, \( \text{Al}_2\text{O}_3 \) and \( \text{NiO} \) are relatively corrosion-resistant pure oxides.

REFERENCES:

POTASSIUM OXIDE

\[ 2K + \frac{1}{2}O_2 = K_2O \]

According to Zintl, Harder and Dauth, K\(_2\)O is best prepared in the following way. Metallic K is repeatedly remelted under xylene to remove high-boiling oils. It is next degassed by double distillation in a Pyrex tube connected to a vacuum pump and finally filtered under high vacuum through a capillary into a Vycor boat. Thoroughly purified dry air is admitted in small quantities to the mildly heated bright metal. The oxide as finely divided particles absorbs the unreacted metal, liquefied by the heat of reaction, like a sponge. A mass having a mosslike structure and a metallic sheen is obtained. Only a portion of the K is thus oxidized at one time (to prevent peroxide formation). The excess metal is distilled off in high vacuum at 350\(^\circ\)C. The K\(_2\)O which remains in the boat is free of peroxide and is at least 99.5\% pure.

PROPERTIES:

Loose powder, yellow when hot but white at room temperature. Deliquescent in air. Reacts vigorously with H\(_2\)O. At 350–400\(^\circ\)C disproportion into K\(_2\)O\(_3\) + K. d. (x-ray) 2.33. CaF\(_2\) lattice (Cl).

REFERENCES:

RUBIDIUM OXIDE

I.

\[ 2Rb + \frac{1}{2}O_2 = Rb_2O \]

171.0 16.0 187.0

According to Helms and Klem, Rb\(_2\)O is prepared by the same method as K\(_2\)O. The metal is reacted in a glass apparatus with a quantity of O\(_2\) insufficient to prevent peroxide formation. The excess metal is then distilled off.

II.

\[ 2Rb + HgO = Rb_2O + Hg \]

171.0 216.6 187.0 200.6

Another way to prepare Rb\(_2\)O is to react the metal with less than the stoichiometric quantity of HgO. The metal vapor must be distilled into the HgO in small portions to reduce the intensity of the reaction. After the preparation has been held 12 hours at 200\(^\circ\)C,
the excess Rb and the Hg formed in the reaction are distilled off in high vacuum at about 200°C. The Rb₂O remains.

PROPERTIES:

Colorless powder at room temperature, yellow when heated. Decomposed by light, turning dark. Vigorous reaction with H₂O. Above 400°C disproportionates into Rb₂O₂ + Rb. d. (x-ray) 3.72. CaF₂ lattice (C1).

REFERENCES:


CESIUM OXIDE

\[ 2\text{Cs} + \frac{1}{2}\text{O}_2 = \text{Cs}_2\text{O} \]

265.8  16.0  281.8

According to Helms and Klemm, the reaction of Cs with HgO cannot be used to prepare pure Cs₂O. Instead, in a procedure identical to that described for K₂O and Rb₂O, metallic Cs is incompletely oxidized and the excess metal is distilled away in high vacuum at 200°C. Care must be taken that no cesium diffuses back into the Cs₂O during cooling.

Brauer has described an apparatus for the preparation of Cs₂O, shown in Fig. 270. Boat α is shaped like a slipper so that it is able to contain liquid Cs in both vertical and horizontal positions. A nitrogen stream is passed through the horizontal reactor tube, which is open at the ground glass joint. A weighed ampoule, fastened to a wire and filled with pure Cs, is inserted into the reactor tube as shown. Prior to its insertion, the pointed end of the ampoule is scratched a little and tapped with a hot glass rod, so that it may be broken off later on. After insertion, the point is broken off, with the ampoule at H and under a N₂ blanket. The broken off piece of glass is removed. The tube is then set vertically, the ampoule suspended inside, and a ground cap put on. Next the tube is evacuated and the Cs is transferred into the boat by careful melting. After cooling, the empty ampoule is pulled out (still under a stream of N₂) and reweighed. Electrolytic O₂ is measured out by means of a glass burette (using Hg as the sealing
liquid), the amount introduced being insufficient for complete oxidation of the Cs to Cs$_2$O. The oxygen is added to the reaction tube through a short capillary tube, which had been thoroughly evacuated during the evacuation of the main reactor tube. On its way from the burette to the reactor, the oxygen passes through a small U tube, cooled to a low temperature in order to condense the Hg and H$_2$O. Before entering the burette, the O$_2$ is purified by passing through a cotton filter, a layer of palladium asbestos heated to 400°C, and a low-temperature trap.

The oxidation begins as soon as O$_2$ reaches the Cs. To avoid an excessively vigorous reaction, the tube is cooled and the O$_2$ is admitted in small portions. The product develops a brown-black color, and then becomes liquid, but resolidifies as the oxidation proceeds. To keep it liquid, which ensures a more thorough reaction, the cooling is stopped. When conditions warrant it, some heat is applied, but care must be taken to prevent the Cs from evaporating. Finally, the excess Cs is slowly distilled off, with the tube in the horizontal position and the furnace over the tube. The Cs is allowed to condense in portion δ of the tube, which is enclosed in a cardboard box filled with solid CO$_2$. After the bottom end of the tube is broken off at σ, the boat containing the pure Cs$_2$O is transferred to another vessel under a blanket of nitrogen.

**PROPERTIES:**

Orange, but dark in transmitted light. Habit: according to Helms and Klemm, matted needles; according to Brauer, soft laminae cleaved along the base. d. (x-ray) 4.68. Probably has a CdI$_2$ lattice (C6). M.p. (dec.) about 490°C. Deliquescent in air. Vigorous reaction with water (ignites), less violent with alcohol.

**REFERENCES:**

E. Rengade, Compt. Rend, Hebd. Séances Acad. Sci. 144, 753 (1907);

**Lithium and Sodium Peroxides**

Li$_2$O$_2$ and Na$_2$O$_2$

**LITHIUM PEROXIDE**

\[
2 \text{LiOH} + \text{H}_2\text{O}_2 = \text{Li}_2\text{O}_2 + 2 \text{H}_2\text{O}
\]

According to Pierron, Li$_2$O$_2$ is prepared by treating a boiling, saturated solution of LiOH in 95% alcohol with the stoichiometric
quantity of Perhydrol. The solution is decanted from the precipitate. The latter is boiled twice (30 minutes each time) in 95% alcohol, separated, and then dried overnight in vacuum over P₂O₅. The product contains 99.4% Li₂O₂. Starting with 10 g. of LiOH, 5-6 g. of Li₂O₂ is obtained. The Li in the alcoholic mother liquor can, however, be reused.

Very pure Li₂O₂ can easily be obtained from Li₂O₂, which can initially contain Li₂O for this purpose, by heating in a glass tube at 300°C in vacuum. Pure Li₂O forms in theoretical amounts as a perfectly white powder.

PROPERTIES:

d. 2.14. Structure: probably similar to Hg(I) halides (D₃ᵥ type).

SODIUM PEROXIDE

\[
2 \text{Na} + \text{O}_2 = \text{Na}_2\text{O}_2
\]

46.0 32.0 78.0

In preparing Na₂O₂ it is advantageous to oxidize metallic Na to Na₂O in an atmosphere containing less O₂ than air. The Na₂O is then oxidized completely to Na₂O₂ in an atmosphere containing more O₂ than air, at temperatures ranging from 200 to 350°C. If the Na₂O is ground before the second oxidation step (to facilitate the reaction), air moisture must be excluded during grinding and reaction.

PROPERTIES:

Yellowish. M.p. 460°C (does not decompose). Forms H₂O₂ with H₂O. At red heat decomposes, evolving O₂. d. 2.47. Structure probably similar to Hg(I) halides (D₃ᵥ type).

REFERENCES:
F. Fehér, Angew. Chem. 51, 497 (1938).

Alkali Dioxides

NaO₂

\[
\text{Na}_2\text{O}_2 + \text{O}_2 = 2\text{NaO}_2
\]

78.0 32.0 110.0

In the method of Stephanou, Schlechter, Argersinger and Kleinberg, 92% pure Na₂O is prepared by the action of O₂ on Na₂O₂ at
\~500\degree C and 300 atm. A high-grade steel bomb (180-ml. capacity) provided with a thermocouple is connected through a needle valve to a vacuum pump and an oxygen cylinder. A weighed amount (about 10 g.) of very pure \( \text{Na}_2\text{O}_2 \), free from carbonate, is placed in an open Pyrex vessel and introduced into the bomb. After evacuating for several hours at 1-3 mm., enough \( \text{O}_2 \) is pumped to raise the initial pressure in the bomb to about 300 atm. when the latter is heated to 500\degree C. The valve is then closed. When no further pressure drop is noted, indicating that the reaction has been completed (in 100 hours, at the most), the bomb is left to cool. The fused product is readily powdered in the absence of moisture.

\( \text{KO}_2, \text{RbO}_2 \) and \( \text{CsO}_2 \)

\[
\text{K} (\text{Rb, Cs}) + \text{O}_2 = \text{KO}_2 (\text{RbO}_2, \text{CsO}_2)
\]

According to Klemm and Sodomann, as well as Helms and Klemm, the best method for preparing \( \text{KO}_2, \text{RbO}_2 \) and \( \text{CsO}_2 \) is by oxidation of the elements, dissolved in liquid \( \text{NH}_3 \), with \( \text{O}_2 \) at \(-30\) to \(-50\degree C\). Intermediate products appear first. Their color is light yellow when fresh, then dark. Finally, yellow dioxides are formed. To prevent an explosion, which is common in this reaction, Lux and Kuhn suggest the following procedure, using \( \text{K}_2\text{O} \) as an example.

Ammonia gas, predried with KOH, is first passed for 2-3 hours through reaction vessel \(
\alpha
\) (Fig. 271) until all of the \( \text{O}_2 \) is displaced. An acetone-Dry Ice bath (about \(-50\degree C\)) is then placed under the vessel. The circular copper channel \( \gamma \) is fitted tightly around the upper third of \( \alpha \). It is filled with an acetone-Dry Ice mixture at \(-70\) to \(-80\degree C\). As soon as the lower third of reaction vessel \( \alpha \) is filled with liquid \( \text{NH}_3 \), a piece of potassium is placed in the adapter \( \alpha \) and carefully melted by electrical heating. The reasonably pure metal trickles through capillary \( \beta \) (diameter about 1 mm.) into the liquid \( \text{NH}_3 \). Spattered \( K \), which might easily cause an explosion, is completely washed off the walls by refluxing \( \text{NH}_3 \), using channel \( \gamma \) as a reflux condenser.

After all the \( K \) is dissolved, adapter \( \gamma \) is quickly replaced with a plain cap \( \gamma \). The stopcock is then quickly switched over to
admit $O_3$, prepurified with soda-lime, $CaCl_2$ and $P_2O_5$. A white precipitate of $K_2O_3$ appears first, followed by a brick-red intermediate product (possibly $K_2O_3$). The latter is finally converted to yellow $KO_2$. After about four hours, the coolant is removed and all remaining $NH_3$ is evaporated in a stream of $O_2$. Finally, the freshly formed $KO_2$ is heated, in an oil-pump vacuum, with a non-luminous flame and transferred to a suspended collector tube. The oxygen content of the preparation is close to theoretical.

PROPERTIES:

Yellow substances, decomposed by $H_2O$ with evolution of $O_2$. The structure of $NaO_2$ is similar to that of $NaCl$, with $O_2$ replacing the $Cl^-$ ions. Structures of $KO_2$, $RbO_2$ and $CsO_2$: $CaC_2$ lattice (C11).

<table>
<thead>
<tr>
<th>Structure</th>
<th>d,(x-ray)</th>
<th>M.p.,°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NaO_2$</td>
<td>2.21</td>
<td>—</td>
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<tr>
<td>$KO_2$</td>
<td>2.14</td>
<td>380</td>
</tr>
<tr>
<td>$RbO_2$</td>
<td>3.06</td>
<td>412</td>
</tr>
<tr>
<td>$CsO_2$</td>
<td>3.80</td>
<td>432</td>
</tr>
</tbody>
</table>

REFERENCES:


**Lithium Hydroxide**

$LiOH \cdot H_2O$, $LiOH$

$$Li_2SO_4 + Ba(OH)_2 \cdot 8 H_2O = 2 LiOH \cdot H_2O + BaSO_4 + 6 H_2O$$

$$\begin{array}{c|c|c|c}
\text{Molar Weight} & 109.9 & 315.5 & 83.9 & 233.4 \\
\text{LiOH} \cdot H_2O & 42.0 & 24.0 & 18.0 \\
\end{array}$$

To prepare lithium hydroxide by the method of Barnes, equivalent amounts of aqueous solutions of $Li_2SO_4$ and $Ba(OH)_2$ are
reacted and the filtrate is concentrated in vacuum on a Pt dish. The product solution tends to become supersaturated. It takes three weeks before large needle-shaped crystals of the monohydrate LiOH · H₂O are formed.

According to De Forcrand, the powdered monohydrate is converted to LiOH on drying for several days over P₂O₅ in vacuum. The dehydration can also be accomplished by slow heating of the monohydrate of 140°C in a silver boat, white in a stream of pure H₂. If the temperature is raised too rapidly, the preparation melts at 445°C and converts to a hydrate 8LiOH · H₂O, which can be dehydrated only with difficulty. At 660-780°C the compound loses all its water and Li₂O remains as a residue.

PROPERTIES:

LiOH: white, translucent, less hygroscopic than NaOH. M.p. 462°C. d. 1.46 B10 structure type.
LiOH · H₂O: a saturated solution at 25°C contains 7.15% Li₂O. d. 1.51 B36 structure type.

REFERENCES:


Rubidium and Cesium Hydroxides

RbOH, CsOH

\[
\text{Rb}_2\text{SO}_4 (\text{Cs}_2\text{SO}_4) + \text{Ba(OH)}_2 = 2 \text{RbOH (CsOH) + BaSO}_4
\]

267.0 (361.9) 171.4 205.0 (299.8) 233.4

To prepare RbOH and CsOH according to Barnes, aqueous solutions of Rb₂SO₄ (or Cs₂SO₄) and Ba(OH)₂ are reacted in equivalent proportions. The filtrate is concentrated in a Pt dish in vacuum over solid KOH and heated slowly at 300°C in a silver boat in a stream of CO₂ free hydrogen.

According to Von Hevesy, the last persistently adhering traces of water are removed by bubbling through purified and dried N₂ through the melt with the aid of a thin Ag tube.

According to Winslow, Liebhafsky and Smith, pure RbOH and CsOH are prepared by electrolysis of the chlorides, using an amalgam procedure carried out in a multicell apparatus.

The hydroxides can be worked up to the azides, chromates and iodides.
PROPERTIES:

White, crystalline, very hygroscopic substances. RbOH and CsOH: m.p. 301°C and 272.3°C. Enantiotropic transformation points 245°C and 223°C. Saturated aqueous solutions at 30°C contain 65.56% Rb₂O and 70.63% Cs₂O. Soluble in alcohol. d. 3.20 and 3.675.

REFERENCES:

G. von Hevesy, Z. phys. Chem. 73, 667 (1910).

**Lithium Nitride**

\[ \text{Li}_3\text{N} \]

\[ 3\text{Li} + \frac{1}{2}\text{N}_2 = \text{Li}_3\text{N} \]

20.8 14.0 34.8

The method of Zintl and Brauer uses pieces of pure Li milled clean under an Ar blanket. These pieces are then transferred in the absence of air to a vessel described by Zintl and Woltersdorf (Fig. 272) and nitrided. The crucible \( t \) is made of zirconium dioxide coated with fused lithium fluoride (m.p. 840°C). In contrast to most ceramic and metal vessels, these crucibles are completely resistant to liquid Li up to 800°C, thus allowing the preparation of pure Li compounds from the metal. Crucible \( t \) is set inside an iron protective crucible \( e \), which is placed in a ceramic tube \( r \). The top adapter \( \varrho \) is cemented to \( r \) with sealing wax. A lead cooling coil is wrapped around the cemented area. Stopcock \( h \) may be used both as a vacuum connection and a gas inlet. A peephole \( g \) cemented onto \( \varrho \), permits observation of the material in the crucible.

Large crystallites are more likely to be obtained if the nitriding is started at 400°C, the temperature is gradually raised to 800°C, and the thoroughly purified and dried \( \text{N}_2 \) is diluted with about 20 vol. % Ar.

Fig. 272. Preparation of lithium nitride: \( t \) crucible made of \( \text{ZrO}_2 \) coated with \( \text{LiF} \); \( e \) iron protective crucible; \( r \) ceramic outer tube; \( \varrho \) glass adapter with a glass peephole \( g \) and stopcock \( h \).
PROPERTIES:

Ruby-red, translucent crystallites, decomposed by moisture with evolution of \( \text{NH}_3 \). d. (x-ray) 1.28. Hexagonal.

REFERENCES:


**Phosphides, Arsenides, Antimonides and Bismuthides**

of Alkali Metals from the Elements

<table>
<thead>
<tr>
<th></th>
<th>F  31.0</th>
<th>As 74.9</th>
<th>Sb 121.8</th>
<th>Bi 209.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>20.8</td>
<td>Li(_3)P 50.8</td>
<td>Li(_3)As 95.7</td>
<td>Li(_3)Sb 142.6</td>
</tr>
<tr>
<td>Na</td>
<td>69.0</td>
<td>Na(_3)P 99.0</td>
<td>Na(_3)As 143.9</td>
<td>Na(_3)Sb 190.7</td>
</tr>
<tr>
<td>K</td>
<td>117.3</td>
<td>K(_3)As 192.2</td>
<td>K(_3)Sb 239.0</td>
<td>K(_3)Bi 326.3</td>
</tr>
</tbody>
</table>

According to Brauer and Zintl, the phosphides, arsenides, antimonides and bismuthides of Li, Na and K are prepared as follows.

**Preparation of starting materials:** Alkali metals stripped of crusts under light benzine, then freed of the latter in high vacuum; red phosphorus prepared from freshly distilled, completely dry yellow phosphorus by prolonged heating at 275°C; As, sublimed in a nitrogen stream; Sb and Bi of highest purity (see also the related sections of this book).

\( \text{Li}_3\text{P}, \text{Li}_3\text{As}, \text{Li}_3\text{Sb} \) and \( \text{Li}_3\text{Bi} \)

To prepare \( \text{Li}_3\text{P} \) (or \( \text{Li}_3\text{As} \)), Li and red P (or Li and As) are fused in a crucible made of zirconium dioxide and lined with LiF (see under \( \text{Li}_3\text{N} \)). The crucible is hermetically sealed in an iron crucible and heated to 680°C for \( \text{Li}_3\text{P} \) and to 800°C for \( \text{Li}_3\text{As} \). Very pure red-brown \( \text{Li}_3\text{P} \), or brown-black \( \text{Li}_3\text{As} \), is obtained. It is transferred from the crucibles to glass vessels provided with ground stoppers and stored under Ar. The product should not come in contact with air at any time.

To obtain \( \text{Li}_3\text{As} \) and \( \text{Li}_3\text{Sb} \), a suspension of freshly powdered As (or Sb) in anhydrous liquid \( \text{NH}_3 \) is prepared. A solution of Li in dried liquid ammonia is added, in small portions, to the suspension. The reaction begins on shaking. Its termination is indicated by the appearance of a blue color in the supernatant fluid, due to a slight excess of Li. The \( \text{NH}_3 \) is boiled out, with the last
traces removed by vacuum. The products are either the brown Li$_3$As powder (very air sensitive; must be stored under pure N$_2$ or Ar) or blue-gray $\beta$-Li$_3$Sb powder. The particle size of the latter can be increased by heating at 650°C. Another modification, $\alpha$-Li$_3$Sb, is obtained by quenching of the melt (m.p. between 1150 and 1300°C) under Ar in a thick-walled iron crucible with welded-on lid.

According to Zintl and Brauer, Li$_3$Bi is prepared by melting together stoichiometric quantities of Li and Bi in tall, narrow iron crucibles, followed by slow cooling. The crucibles are filled with Ar and tightly closed with welded-on iron stoppers. (See also Part III, section on intermetallic compounds.)

Na$_3$P, Na$_3$As, Na$_3$Sb and Na$_3$Bi

The phosphide forms when stoichiometric quantities of Na and red P are fused under a protective Ar blanket in a Tamman crucible. The latter is made of sintered corundum and is hermetically sealed in an outer iron crucible.

To prepare Na$_3$As, Na vapor is passed over heated As. An iron boat filled with Na is placed inside an evacuated Vycor tube, together with another boat made of sintered corundum and filled with As powder. Using small movable electric tubular heaters, the Na is vaporized at 350–450°C and the vapor is passed over the As, preheated to 180–200°C. Conversion to brown-violet Na$_3$As is complete. The excess Na is removed from the apparatus on heating to 450°C in high vacuum.

Both Na$_3$Sb and Na$_3$Bi are obtained from stoichiometric quantities of the respective reactants which are melted together in tall, narrow crucibles (filled with Ar and tightly closed with welded-on iron stoppers) at temperatures exceeding the melting point (856°C and 775°C, respectively) by 50–100°C. (See the section on Intermetallic Compounds, Part III.) After slow cooling, the crucibles are cut open under a protective gas blanket. The products are brittle, bluish or violet-gray, and have a slight metallic sheen.

K$_3$As, K$_3$Sb and K$_3$Bi

The arsenide is obtained in a manner analogous to Na$_3$P at 800°C. It is a very brittle substance with a greenish metallic luster.

Both K$_3$Sb and $\alpha$-K$_3$Bi are prepared in the same manner as the corresponding Na compounds (m.p. 812°C for K$_3$Sb and 671°C for K$_3$Bi). Both substances are very brittle, with a green-yellow sheen resembling that of fuchsin crystals ($\beta$-K$_3$Bi is stable only above 280°C).
18. ALKALI METALS

PROPERTIES:

β-Li₃Sb and Li₃Bi crystallize in DO₃ structure type; all the others, in type DO₁₃. D. (x-ray): Li₃P 1.43; Li₃As 2.42; α-Li₃Sb 2.96; β-Li₃Sb 3.29; Li₃Bi 5.03; Na₃P 1.74; Na₃As 2.36; Na₃Sb 2.67; Na₃Bi 3.70; K₃As 2.14; K₃Sb 2.35; K₃Bi 2.98.

REFERENCES:


Sodium and Lithium Carbides

Na₂C₂, Li₂C₂

\[
\begin{align*}
2 \text{Na} (\text{Li}) + 2 \text{C}_2\text{H}_2 &= 2 \text{NaHC}_2 (\text{LiHC}_2) + \text{H}_2 \\
46.0 \ (13.9) &+ 52.1 \quad 96.1 \ (63.9) \quad 2.0 \\
2 \text{NaHC}_2 (\text{LiHC}_2) &= \text{Na}_2\text{C}_2 (\text{Li}_2\text{C}_2) + \text{C}_2\text{H}_2 \\
96.1 \ (63.9) &+ 70.0 \ (37.9) \quad 26.0
\end{align*}
\]

In the method of Antropoff and Müller, Na₂C₂ may be prepared by letting acetylene react with Na dissolved in liquid NH₃. The sodium acetylide thus formed loses acetylene at 145°C in vacuum and is converted to Na₂C₂. The latter is obtained as a pure white product, containing 1.3-3.0% undecomposed acetylide.

Lithium carbide, obtained in a similar way, invariably contains 20% acetylide, even when heated in vacuum to the decomposition temperature of the carbide (about 300°C).

PROPERTIES:

Na₂C₂ is very hygroscopic. d. 1.575. Li₂C₂ is white and crystalline; decomposed by water. d. 1.65.

REFERENCES:


Alkali Metal Carbonates of Highest Purity

To purify commercial Li₂CO₃ (as well as lithium carbonate obtained from minerals), it is dissolved in acetic acid, following
the method of Zintl, Harder and Dauth; the Ca is precipitated with ammonium oxalate and the Mg with Ba(OH)$_2$ solution. The barium is removed from the filtrate by precipitation with sulfuric acid. The solution, separated from the precipitate, is evaporated to dryness and the residue mildly calcined to remove ammonium salts. It is then dissolved in hydrochloric acid and treated with distilled ammonium carbonate to precipitate pure Li$_2$CO$_3$.

Pure Na$_2$CO$_3$, K$_2$CO$_3$, Rb$_2$CO$_3$ and Cs$_2$CO$_3$ are prepared by the method of Suhrmann and Clusius, starting with pure alkali chlorides. These salts are converted to the nitrates by treatment with excess nitric acid in steamed-out Pyrex vessels. After removal of the chlorine, the nitrates are treated in a Pt dish with a fourfold amount of crystallized oxalic acid and are finally calcined to the pure carbonates. No foreign metals are used in this method; hence no impurities can be introduced.

PROPERTIES:

Li$_2$CO$_3$: formula weight 73.9. Colorless monoclinic crystals. M.p. 735°C, b.p. 1200°C. Solubility at 0°C, 1.54; at 20°C, 1.33; and at 100°C, 0.73 g./100 g. of H$_2$O. d. 2.1.

Na$_2$CO$_3$: formula weight 106.0. Transition point 450°C. m.p. 860°C. Solubility at 20°C (solid phase Na$_2$CO$_3$ · 10H$_2$O), 21.58 g.; at 35°C (solid phase Na$_2$CO$_3$ · 7H$_2$O), 49.25 g.; and at 75°C (solid phase Na$_2$CO$_3$ · H$_2$O), 45.88 g./100 g. of H$_2$O. CO$_2$ pressure 1 mm. at 700°C. d. 2.53.

K$_2$CO$_3$: formula weight 138.2. Transition point 140°C. m.p. 891°C. Hygroscopic. Solubility at 0°C, 105 g.; at 20°C, 112 g.; and at 100°C, 156 g./100 g. of H$_2$O. CO$_2$ pressure 1.2 mm. at 950°C. d. 2.43.

Rb$_2$CO$_3$: formula weight 231.0. m.p. 837°C. On melting, attacks Pt. Very hygroscopic. Solubility in water at 20°C, 69.01 g./100 g. of saturated solution. Solubility in absolute alcohol at 19°C, 0.74 g./100 g. of alcohol. CO$_2$ pressure 2 mm. at 740°C; 10 mm. at 900°C.

Cs$_2$CO$_3$: formula weight 325.8. Melts at red heat. Deliquescent in air. Solubility in H$_2$O: at 20°C, the saturated solution contains 72.34% Cs$_2$CO$_3$. Solubility in absolute alcohol at 19°C, 11.1 g./100 g. of alcohol; at the b.p. of alcohol, 20.1 g. CO$_2$ pressure 2 mm. at 610°C; 44 mm. at 1000°C.

REFERENCES:

Silicides and Germanides of Alkali Metals

from the Elements

NaSi, KSi, RbSi, CsSi, NaGe, KGe, RbGe, CsGe

<table>
<thead>
<tr>
<th></th>
<th>+ Si</th>
<th>+ Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>23.0</td>
<td>NaSi</td>
</tr>
<tr>
<td>K</td>
<td>39.1</td>
<td>KSi</td>
</tr>
<tr>
<td>Rb</td>
<td>85.5</td>
<td>RbSi</td>
</tr>
<tr>
<td>Cs</td>
<td>132.9</td>
<td>CsSi</td>
</tr>
</tbody>
</table>

The alkali silicides and germanides are very moisture sensitive. In the method of Hohmann the synthesis is carried out in corundum crucibles set in vacuum-tight, Ar-filled iron bombs (Fig. 273, A and B). The corundum crucible i is thoroughly ignited before being charged with a small amount (a fraction of a gram) of Si (or Ge) which has been finely ground in an agate mortar. Crucible i is then placed in small bomb δ, and the latter set on the stem of a Pyrex device (Fig. 274) designed for transfer of alkali metals. The apparatus is carefully evacuated through c (so as not to lose any Si or Ge through dusting), and Ar gas is let in through the same route and escapes through ε. Next, ampoule f, containing the alkali metal and already opened at the bottom, is introduced through ε and allowed to slide down into the slightly tilted apparatus. Ground cap ε is then replaced and the apparatus is evacuated at once. The area B is then thoroughly heated with a gas burner. The alkali metal (present in a three- or fourfold excess) is caused to flow into the crucible by heating area f with a flame. After cooling, Ar is reintroduced and the bomb removed in a strong Ar stream through the bottom by lifting cap a. The bomb is immediately tightly closed with cone l, ring (or plate) gasket k and screw-cap h (see Fig. 273).

Following completion of the reaction (see below), the bomb is slowly cooled and opened by unscrewing the cap until 0.5 mm. of the thread is left, and then breaking off the cap is on a bench vise. The open bomb is quickly pushed into the distillation tube (Fig. 275), through which either Ar or N₂ is flowing. After evacuating briefly, Ar is again admitted and the tube sealed at m. Finally, an electric furnace is slid over the tube and the excess of alkali metal is separated from the product by distillation in high vacuum and condensed in n. This may take several days. After breaking off the end of the tube at m, bomb b containing the corundum crucible is taken out in a stream of Ar. If necessary, the product can be ground in an apparatus proposed by Klemm and Dinkelacker, in the absence of air and moisture. (See section on Intermetallic Compounds.)
Fig. 273. Iron bombs used in the preparation of alkali metal silicides and germanides: $A$—bomb for preparation of Rb and Cs compounds; $B$—bomb for the Na and K compounds. $b$—iron bomb; $h$—iron screw-on cap; $t$—corundum crucible; $k$—copper gasket; $l$—iron cone.

Fig. 274. Filling (transfer) apparatus for preparing alkali metal silicides and germanides: $b$—iron bomb; $d$—silicon or germanium; $f$—ampoule containing alkali metal.

Fig. 275. Separating the excess alkali metal from the silicide or germanide by distillation.

Supplementary Synthesis Data

<table>
<thead>
<tr>
<th></th>
<th>Optimum reaction temperatures</th>
<th>Reaction time</th>
<th>Distillation temperature time</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaSi</td>
<td>700°C</td>
<td>1-2 days</td>
<td>280-300°C 240-250</td>
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<tr>
<td>KSi</td>
<td>650</td>
<td>4-5 days</td>
<td>4 days several days</td>
</tr>
<tr>
<td>RbSi</td>
<td>600</td>
<td>3-4 days</td>
<td>180-200</td>
</tr>
<tr>
<td>CsSi</td>
<td>600</td>
<td>3-4 days</td>
<td>150-180</td>
</tr>
<tr>
<td>NaGe</td>
<td>650-700</td>
<td>2 days</td>
<td></td>
</tr>
<tr>
<td>KGe, RbGe, CsGe</td>
<td>600</td>
<td>several days</td>
<td></td>
</tr>
</tbody>
</table>
PROPERTIES OF SILICIDES:

Very sensitive to moisture. Reactivity increases from NaSi to CsSi: NaSi self-igniting only as a loose powder; KSi self-igniting with detonation. All four silicides ignite explosively on contact with water or dilute acids. With dilute alkalis the reaction is milder.

NaSi: Long needles, metallic luster.
KSi: Hard, poorly crystallized substance with dark luster.
RbSi: Small dark crystals.
CsSi: Brittle, brass-colored compact mass; also single crystals.

Decomposition temperatures in high vacuum: NaSi 420°C; KSi 360°C; RbSi and CsSi 350–360°C. Decomposition products: Na + Si, KSi, RbSi, and CsSi.

PROPERTIES OF GERMANIDES:

Sensitive to moisture, but less reactive than the silicides. Decompose in air into alkali hydroxide and brown germanium monohydride \((\text{GeH})_x\). Decompose rapidly, with occasional igniting in water, dilute acids or dilute alkalis.

NaGe: Small, well-formed needles, metallic luster.
KGe: Loose, dark-colored substance; no well-defined crystals.
RbGe: Bronze-colored crystals.
CsGe: Crystals of a beautiful jet-black color.

Decomposition temperature in high vacuum: NaGe 480°C; KGe 400–420°C; RbGe and CsGe 390–410°C. Decomposition products: Na + Ge, KGe, RbGe, and CsGe.

\[
\begin{align*}
2 \text{Li} (4 \text{Li}) + \text{Si} &= \text{Li}_2\text{Si} (\text{Li}_4\text{Si}) \\
13.9 &\quad (27.8) \\
28.1 &\quad 41.9 \quad (55.8)
\end{align*}
\]

In the method of Klemm and Struck, \(\text{Li}_2\text{Si}\) and \(\text{Li}_4\text{Si}\) are prepared in small tubular nickel crucibles. These are charged with weighed amounts of Si and Li in the absence of air and moisture and heated under argon in a Thermax steel bomb provided with a screw-on cap. The reaction temperature for \(\text{Li}_2\text{Si}\) is 530°C and for \(\text{Li}_4\text{Si}\), 630°C. After cooling, the products can be ground, if needed, in an apparatus proposed by Klemm and Dinkelbacker. (See section on Alloys and Intermetallic Compounds.)

PROPERTIES:

Sensitive to moisture. \(\text{Li}_2\text{Si}\) is dark violet; \(\text{Li}_4\text{Si}\) is silver-gray.
REFERENCES:

L. M. Dennis and N. A. Skow, J. Amer. Chem. Soc. 52, 2369 (1930).