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Alkali Hydrides

NaH, KH, RbH, CsH and LiH

$$\underset{6.9\ (23.0;\ 39.1;\ 85.5;\ 132.9)}{\text{Li (Na, K, Rb, Cs)}} + {}^1/_2\,H_2 = \underset{7.95\ (24.0;\ 40.1;\ 86.5;\ 133.9)}{\text{LiH (NaH, KH, RbH, CsH)}}$$

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 *a* is inserted into a quartz or Vycor tube *r* as protection against corrosion by alkali metal vapors. Liner *a* is preheated for many hours in moist H_2 at 900°C to decarbonize the steel. As iron boat *c* is placed in sheet iron cylinder *b*, which is closed on one side. After prolonged evacuation of the apparatus the surfaces of *a*, *b* and *c* are deoxidized by passage of electrolytic H_2 (inlet at *h* and outlet at the loosely fitting joint s_1) and simultaneous prolonged heating of *a*, *b* and *c* to dull red heat, using an electric oven.

The electrolytic H_2 must be very thoroughly freed of O_2 and H_2O and before entering the reaction zone must pass through a large U tube filled with resublimed P_2O_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 *c*.

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_2CO_3 or Cs_2CO_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 *b* with boat *c* 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 *a*. After cooling, tube *b* with boat *c* containing impurities and/or residues are pulled out from the reaction zone (still under a H_2 stream) through ground glass joints s_2. With manometric valve *v* reconnected, the air is displaced with

H_2 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 H_2 to keep the pressure at 1 atm. When the manometric valve v shows no further pressure drop over a period of 24 hours, the hydride is removed (under a hydrogen stream) from a by pushing it into tube d 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 H_2.

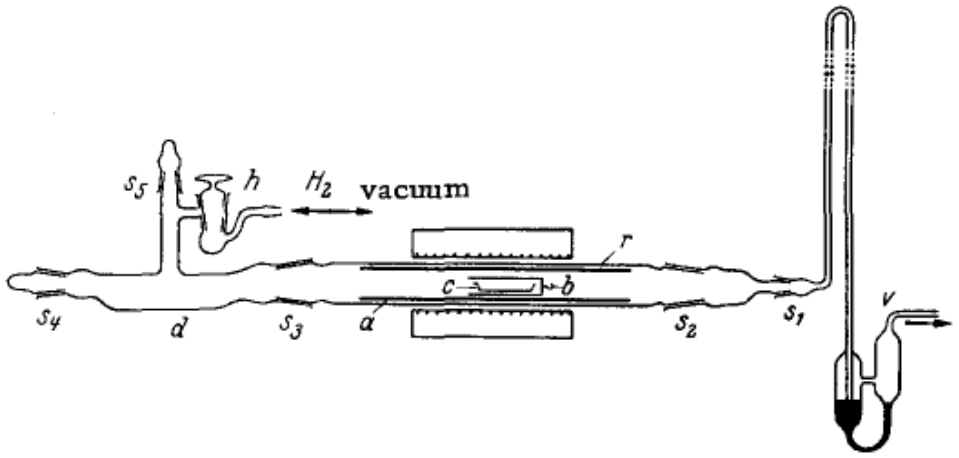

Fig. 268. Preparation of alkali metal hydrides; *r*) quartz or Vycor reaction tube; *a*) protective iron liner; *b*) boat-shielding iron cylinder; *c*) iron boat.

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 H_2 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 H_2 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 H_2 would be lost through hydrogenation of the dispersing medium.

When the 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 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 *a*. 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 *d* 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 *d* 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 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 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 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° 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.

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Alkali Metal Oxides

Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O

LITHIUM OXIDE

$$\underset{73.9}{Li_2CO_3} = \underset{29.9}{Li_2O} + \underset{44.0}{CO_2}$$

Zintl, Harder and Dauth prepared Li_2O by thermal decomposition of pure Li_2CO_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.