

PRODUCTION OF HIGH PURITY CAESIUM

FRITZ BLATTER and ERNST SCHUMACHER

Institute for Inorganic, Analytical and Physical Chemistry, University of Bern, Freiestrasse 3, CH-3012 Bern (Switzerland)

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Summary

High purity caesium is prepared by azide decomposition, a method first described by Suhrmann and Clusius in 1926. All the necessary details are given for the preparation of pure caesium azide from caesium carbonate, and for the proper control of the thermolysis to caesium *in vacuo*. Product purity is assessed using Guinier X-ray and atomic absorption spectroscopy. Caesium of purity 99.998% was obtained, the contaminants being other alkali metals, further removable by distillation.

1. Introduction

Owing to their high chemical reactivity and the resultant problems of their handling, alkali metals are not easily prepared in very high purity. Caesium, rubidium and liquid 1:1 mixtures like NaK spontaneously burn in air and explode in contact with water; safe handling of these metals, therefore, needs a lot of care and precautions. The knowledge of many experimental details is useful and important.

For laboratory use and larger scale production, the literature contains very few publications concerning the preparation of high purity caesium and rubidium (and of the other alkali metals) [1 - 3]. The commercial sources for these metals do not meet the requirements for many applications.

The existing methods are typically not well documented. It is usually left to the experimental chemist's intuition to find out the many subtle details of how to reproduce the experiments and to avoid hazardous situations or the unnoticed introduction of contaminants. This has led to an underdeveloped state of knowledge about the heavy alkali metals proper whereas their salts are well documented. An interesting use requiring extremely high purity caesium arises from the definition of the second as the SI unit of time as 9 192 631 770 periods of the transition between the two hyperfine levels of the groundstate of ^{133}Cs . This transition is measured in a caesium molecular beam which has to be maintained in caesium atomic clocks for several years without replenishing the supply (manufactured by

Oscilloquarz S.A., Neuenburg, Switzerland). The requirements for this application were in fact the main reason for our investigation of the methods for the preparation of caesium. In addition we are interested in metal-cluster research [4] based around the alkalis as the simplest metals well understood by solid state physics. Unusual chemical reactions of caesium found in the course of that work will be published elsewhere.

We restrict ourselves in this paper to the preparation of caesium. This is the most difficult case. The other alkali metals, except lithium, can be prepared similarly. We choose the method first described by Suhrmann and Clusius (1926) [1, 2] for caesium. The metal is obtained by thermal decomposition of caesium azide followed by distillation under high vacuum. Other well-known syntheses for caesium are less suitable for our requirements; small amounts of the metal, e.g. for photocathodes, are obtained by the reduction of $\text{Cs}_2\text{Cr}_2\text{O}_7$ with zirconium powder. Both ingredients can be thoroughly mixed, pressed into a pill and exposed to high temperature in an evacuated environment when the metal is needed. This method is unsuitable for the production of several grams and for very pure caesium. Control of purity is also precarious for several methods starting from caesium hydroxide and using either magnesium or calcium as the reductant *in vacuo* or in a stream of hydrogen gas. Hydroxides are unsuitable compounds for high purity chemistry. Reduction of chlorides with magnesium or calcium is often used for small amounts [4] of alkalis. The reaction is violent and not applicable for use in a glass apparatus.

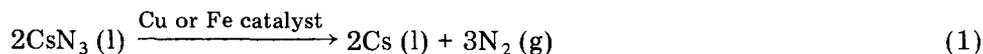
2. Preparation and some properties of the alkali metal azides

The properties of the azides of several metals are well documented [5]. Methods for the preparation, determination of structural and thermodynamic parameters, IR and optical absorption spectroscopy, thermal, photochemical and shock-wave decomposition are described. Although there has been some work on the decomposition of the alkali azides [6 - 8], the process of thermolysis is not well understood. Sears and Steinberg [6] claim that decomposition is accelerated by the presence of Cs_2O_2 and Egghart [9] attributes a similar effect to transition metals. The azides of potassium, rubidium and caesium can easily be prepared by neutralizing the corresponding carbonates with hydrazoic acid. A lower limit for the terminal pH of this neutralization can be calculated from a consideration of the solution equilibria [10]. The number obtained is 7.12 if loss of CO_2 during the neutralization process is neglected.

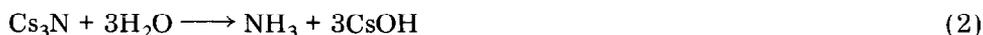
3. Thermal decomposition of alkali azides

The rate of decomposition is a function of temperature but many other factors influence it also, e.g. crystal size, purity, quantity, the walls

of the reaction vessel etc. Therefore, specifying a generally valid decomposition temperature is problematical; the decomposition of pure CsN_3 is very slow even at 500°C whereas 15 g are decomposed at 380°C in less than 1 h if a few small chips of stainless steel, copper or brass are added.



Caesium nitride is formed as a byproduct in very small quantities, which can be verified by the reaction



The colour changes from white to blue-green to yellow during decomposition suggest that intermediate substoichiometric phases CsN_x ($x < 3$) are formed. It is well known that caesium is able to support a large range of metal-rich phases, especially with oxides [11]. The catalysis of thermolysis by heavy metals has often been realized by using a metal reaction thimble blown to a glass vacuum line via a glass-metal seal. The disadvantage of this set-up is the unobservability of the decomposition process and the hazard of breaking the metal-glass seal during several thermal cycles between room temperature and about 450°C during the preparation.

According to the formation enthalpies of the alkali azides in Table 1 the light alkalis are endothermic and decompose at a lower temperature than the heavy ones. This is to be expected for an electron transfer process being favoured by the smaller cation. In order to maintain a smooth, controllable thermolysis, heavy metal catalysis is also recommended for sodium and potassium preparation by this method. Lithium cannot be prepared in a glass apparatus by this process, the glass being destroyed by reduction of the silicate to silicon. In addition thermolysis seems to proceed too violently.

4. Experimental details

4.1. Preparation of the azide

A cation exchange column is half filled with water. 150 g of exchange resin (Dowex 50 WX8, H^+ form, 50-100 mesh; capacity, 1.9 meq ml^{-1} [12],

TABLE 1
Enthalpies of formation for crystalline azides [12, 13]

Azide	ΔH_f° (kcal mol $^{-1}$)
NaN_3	5.1
KN_3	-0.3
RbN_3	-0.1
CsN_3	-4.7

washed free from metal ions by exhaustive elution with azeotropic 6 M HCl) is suspended in 100 ml of distilled water and slowly sedimented on the frit to give a homogeneously packed bed. Then the column is washed consecutively with 1 l distilled water, 500 ml 6 M HCl and then again with distilled water until the eluate is free from chloride ions (test with silver nitrate). The resulting resin is now in the H^+ form and ready for processing. The water level above the resin is reduced to about 1 cm supernatant. To preserve the homogeneous bed the resin must always be kept under a liquid column. A solution of 20 g NaN_3 (0.3 mol) (Merck, pro analysi, 99% pure; solubility in water, $41.7 \text{ g (100 ml)}^{-1}$ at 17°C) in 50 ml H_2O is carefully added from a dropping funnel and the solution is eluted at a rate of one drop per second until hydrazoic acid is detected in the effluent by a pH indicator strip. The column is now in the Na^+ state while the interstitial solution contains hydrazoic acid. This is eluted with distilled water into a platinum dish containing 32.6 g Cs_2CO_3 (Merck, "reinst" quality; purity, 99.8%). The neutralization process is followed by pH measurements, because it cannot be controlled merely by the observation of CO_2 evolution. The titrations were taken to pH 7 which corresponds to a slight excess of hydrazoic acid. The solution is then slowly evaporated by an IR radiator and dried at 110°C (the excess hydrazoic acid decomposes in this process). Owing to the toxicity of hydrazoic acid it is mandatory to work in a well-ventilated hood. The yield is 99% caesium azide. To prevent contamination of the product by sodium only 66% of the column capacity is used. The azide prepared contains traces of low molecular weight polymers of the resin material poly(styrene sulphonate). These are removed by recrystallization of the azide from an ethanol-water mixture.

4.2. Decomposition of the azide (see Fig. 1)

Breakseal ampoules, the cold trap and the ampoules 2 and 3 with the prepared vacuum seals (containing quartz glass wool in 2) are attached horizontally to the vacuum line and held in place with two clamps. The reaction tube 1 is filled with 9 g of CsN_3 (51.5 mmol) and approximately

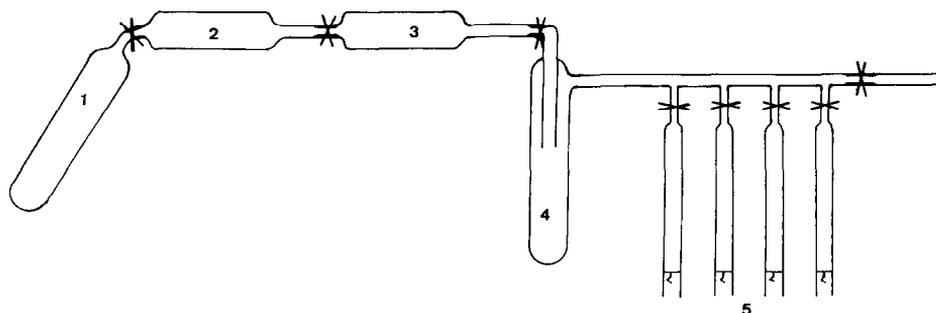


Fig. 1. Glass apparatus for the thermal decomposition of caesium azide: 1, reaction tube; 2, ampoule with quartz wool; 3, ampoule; 4, cold trap; 5, breakseal ampoules; x, prepared seal-offs.

500 mg of stainless steel or copper chips and sealed to ampoule 2. Since the wall thickness of the glass is 1.5 mm, clamps at two points are sufficient. The whole apparatus has to be assembled with great care; thin spots and tension in the glass should be avoided. Subsequently the caesium azide is dried at 300 °C for 12 h under high vacuum, during which time decomposition is minimal. Before the temperature of the oven is raised the apparatus (except the reaction tube) is baked by torch almost to the transition point of the Pyrex glass. If the azide decomposes from the solid rather than from the liquid state (only the case for sodium azide) the apparatus is filled with 200 Torr of dry nitrogen as back pressure to prevent contamination of the breakseal ampoules by azide dust.

The oven is carefully heated to 380 °C; for CsN_3 decomposition begins as low as the melting point (326 °C [1]), the azide starts to “boil” as nitrogen is evolved from the liquid phase. During the reaction liquid azide creeps to the unheated parts of the reaction tube, which can be decomposed by torch. Small quantities of caesium are transferred to ampoules 2 and 3 by the nitrogen stream. The decomposition is complete when the evolution of nitrogen stops, while the oven is slowly heated further to 425 °C. After subsequent cooling to 380 °C the system is evacuated. If the pressure does not drop to lower than 10^{-4} Torr there must still be undecomposed azide in the system. This is left in the reaction tube by distilling caesium into ampoule 2 at 350 °C. Ampoule 1 is sealed off by torch, the product is further purified by distilling it from ampoule 2 to ampoule 3 and finally to the cold trap 4 after having removed ampoule 2. Then ampoule 3 and the whole apparatus with the cold trap and breakseal ampoules are sealed off and the caesium is distributed into the four cooled breakseal ampoules by distillation in the closed system. Azide must not get into the cold trap.

A small quantity (about 500 mg) of a yellow byproduct, mainly nitride, remains in ampoule 1. This reacts vigorously with water (eqn. (2)). The yield of the azide decomposition was determined by two independent methods to be $96.5 \pm 1\%$; compared with 90% [1]. All ampoules are opened and washed with water and can be reused.

5. Discussion

We have given the operational details for a safe, simple and practicable preparation of caesium (and other alkali metals) by the well-known method of azide thermolysis. The resultant purity is sufficient even for the most ambitious applications. The advantages of this method are evident: the starting substances are available or can be made in very good quality; the system consists of a binary salt which decomposes to the product and nitrogen; the catalyst has an extremely low vapour pressure and is removed after decomposition before the rest of the purifying steps. The operation is completely safe even within a much wider temperature range than given in the experimental directives (we tested CsN_3 up to 550 °C without any signs

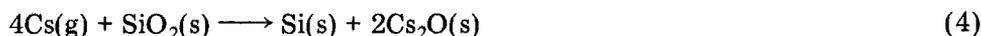
of explosive behaviour). The presence of the catalyst allows a smooth evolution of nitrogen which can be stopped at any time by rapid cooling from the outside (air blower after lowering the oven). In the absence of a catalyst the start of the reaction is about 200 °C higher and the gas evolution more violent and uncontrollable. It is not recommended to proceed without a catalyst even with the important precaution of employing an adequate dead volume in the apparatus to accommodate all the nitrogen formed.

It is advisable to check the chemical nature of the glass vessel coming into contact with the alkali metal. Experiments were done with fused quartz glass, Vycor and Pyrex. All glasses are attacked slightly by caesium above 600 K. A permanent, but weak yellow or brown coloration develops. Fused quartz and Vycor are more reactive than Pyrex. Pyrex contains approximately 5% Na₂O [14, 15]. The exchange of sodium and caesium on the glass surface must, therefore, be considered:



There are no thermodynamic data known to enable precise discussion of this reaction. We substitute carbonates for silicates and evaluate ΔG trends between sodium and caesium compounds [16]. From these we obtain $\Delta G^{600}(\text{reac}) = 0 \pm 10 \text{ kcal mol}^{-1}$ for the above reaction. It is probably quite slow and can be kept to a minimum by distilling caesium at a temperature below 200 °C.

For the reduction of silicon (in glass) by caesium we have



$\Delta G(\text{reac}) = 57.8 \text{ kcal mol}^{-1}$ at 600 K; an unfavourable reaction but one that seems to proceed to an observable extent if it is responsible for the staining of the glass.

Pyrex glass is attacked slightly by strong bases which leads to contamination when caesium metal is hydrolyzed for chemical analysis. The sodium content found after such a process is an upper limit. It is preferable to perform the hydrolysis in a platinum dish.

The azides were characterized by the Guinier X-ray powder method, their purity and that of the caesium were determined by atomic absorption spectroscopy after dissolution. The impurities found were: sodium, less than 2 ppm; potassium, less than 1 ppm; rubidium less than 1 ppm. For boron, lithium and silicon we were only able to determine an upper limit of less than 10 ppb. The golden-yellow caesium metal melts and crystallizes sharply at 28.6 °C.

Using a glass apparatus for higher alkali metal preparation requires some precautions because of the possibility of exchange with the alkali ions in the glass phase as mentioned before. Choice of a glass with low alkali content is recommended. We also used stainless steel thimbles for the azide thermolysis without noticeable improvement in purity. It would, of course, be possible to eliminate glass completely and use an all-metal apparatus. However, transparency allows supervision of the chemical reactions occurring. The

purity of the precursor caesium azide is by far the most decisive factor in determining the quality of the caesium. Hydrazoic acid prepared by ion-exchange with azeotropic hydrochloric acid in a Teflon- or polyethylene column is free from metallic contaminants. In principle HN_3 could be passed through the gas phase into the carbonate and thus would not introduce any metals. Therefore, the starting caesium carbonate alone determines the ultimate purity of the caesium. This is far better than for the other processes used to produce caesium. If necessary caesium can always be further purified from the lower alkalis by high vacuum distillation.

Acknowledgment

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