INORGANIC SYNTHESES

VOLUME I

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INORGANIC SYNTHESES

VOLUME I

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PREFACE

At the Chicago meeting of the American Chemical Society, September, 1933, a group of inorganic chemists decided that there was a vital need for a series of volumes giving detailed and tested methods for the synthesis of inorganic compounds. Lack of space in chemical journals has compelled publication of material in so brief a form that frequently critical details essential to the success of a synthesis have been omitted. As a result, in an attempt to use the published synthesis, an investigator may find it necessary to rediscover the conditions that lead to success.

To meet this need, the group selected L. F. Audrieth, Harold S. Booth, W. Conard Fernelius, Warren C. Johnson, and Raymond E. Kirk, as a board of editors and asked Harold S. Booth to act as editor-in-chief to get the project under way. Later, the board of editors elected John C. Bailar, Jr., to the board.

Each synthesis in this volume has been carefully checked in the laboratory, and usually in a laboratory other than that in which the synthesis was initiated. All directions and procedures have been critically edited by each member of the board of editors with the hope of minimizing errors. The editors will deem it a favor if readers will call their attention to any errors or omissions.

Some of the methods are new, but many are improvements on older procedures. Where it was thought helpful, a critical survey of known methods introduces the synthesis and a summary of the more common properties of the substance concludes the synthesis to guide the user of the method. The references are not intended to be exhaustive.

For convenience, the book is arranged in chapters numbered according to the groups in the Mendeléev

periodic table. A similar arrangement is proposed for subsequent volumes in the series. It is planned to include in Chap. IX of each volume materials and techniques of value to chemists. Future contributions of this kind are solicited by the board of editors.

Professor W. Conard Fernelius, The Ohio State University, Columbus, Ohio, has been selected by the board as editor-in-chief of Volume II of "Inorganic Syntheses." The collection and checking of syntheses for Volume II is now under way and contributions should be sent direct to Professor Fernelius. The board asks contributors to follow the style employed in Volume I, and to submit manuscripts and drawings in *triplicate.*

The editors wish to express their appreciation to those who have contributed and checked the syntheses in Volume I and ask for their continued cooperation. They likewise take this occasion to thank Dr. Roger Adams for his continuous encouragement and interest and for his kindly foreword.

The editor-in-chief wishes to thank his associates for their vigorous enthusiasm and tireless labor in the preparation of Volume I.

H. S. B.

CLEVELAND, OHIO,
March, 1939.

FOREWORD

It is with much satisfaction to all chemists that volumes are now to appear periodically describing satisfactory procedures for the synthesis of various inorganic chemicals. Although the field in inorganic chemistry may not be so extensive as that in organic chemistry, nevertheless it is equally desirable to have a reliable source of information for preparing representative compounds of the elements other than carbon. A real demand is thus to be filled.

The objective is to provide sufficient detail for each preparation so that a chemist of ordinary experience may duplicate the results on first trial. The realization of proper directions has been made possible by checking the syntheses before publication in at least one laboratory other than that of the submitter.

The first volume should assure the success of the endeavor. Many of the preparations given are of the kind for which every laboratory has a need and for which it has been almost impossible to find desirable details for synthesis.

The volumes of "Organic Syntheses" were initiated in 1921 with similar objectives and have been appearing annually since that time. Their general acceptance has indicated their usefulness and has fully justified the laborious undertaking. "Inorganic Syntheses" will no doubt be rewarded with the same success. The past and present editors of "Organic Syntheses" join with other chemists in welcoming this new enterprise.

ROGER ADAMS,
Head of the Chemistry Department

UNIVERSITY OF ILLINOIS,
March, 1939.

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INORGANIC SYNTHESES

CHAPTER I

1. PURIFICATION OF LITHIUM CARBONATE

SUBMITTED BY E. R. CALEY* AND P. J. ELVING*
CHECKED BY WILLIAM D. STILLWELL†

Since lithium salts obtainable by purchase, even of so-called "c.p." or "reagent" quality, frequently contain impurities totaling about 1 per cent, it is desirable to have a rapid method for obtaining such salts in a reasonably pure state. The following simple procedure for the purification of c.p. or reagent grade lithium carbonate provides such a method, since the resulting pure carbonate may be readily converted by treatment with the proper pure acid into practically any lithium salt desired. The procedure is based upon the fact that lithium carbonate, in contrast to the salts that contaminate it, is much less soluble in hot than in cold water.‡ In other words, simple recrystallization is employed, but the process is carried out in the reverse direction.

Procedure

Twenty-five grams of lithium carbonate is dissolved in 2 l. of water in a 3-l. beaker at room temperature. This operation requires about half an hour if stirred by a motor stirrer. Suspended impurities and any small residue of undissolved carbonate are then removed by filtering the solution, preferably through a large folded filter. The

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‡ At 20°C., 1.33 g. of lithium carbonate is soluble in 100 g. of water; and at 100°C., the solubility drops to 0.72 g.

filtrate, in an *unscratched* beaker, is heated gradually almost to the boiling point, vigorous stirring being employed continuously to prevent adhesion of the precipitated lithium carbonate to the walls of the vessel. When precipitation is complete, the hot mixture is filtered at once, preferably through a sintered-glass filtering crucible or funnel, and the carbonate is washed two or three times with small volumes of boiling water. The salt is dried at 110°C.

The yield, based on the amount of lithium carbonate taken, is about 40 per cent. The filtrate from the second filtration may, after cooling, be again saturated with lithium carbonate to give a second crop almost as pure as the first. In this way, the total yield can be considerably increased.

For special purposes, where a product of higher purity is required, a double recrystallization from hot water may be employed; but in this case, of course, the yield is considerably reduced.

From a crude lithium carbonate containing 0.78 per cent SO_4 and 0.54 per cent foreign alkali (calculated as Na) three lots of purified lithium carbonate containing 0.03, 0.08, and 0.07 per cent foreign alkali and only traces of sulfate were obtained. The third lot was obtained by crystallizing lithium carbonate from the filtrate from a previous treatment.

2. PURIFICATION OF SILVER RESIDUES

$$2AgNO_3 + 2NH_4CHO_2 \rightarrow 2Ag + CO_2 + 2NH_4NO_3 + HCHO_2$$

SUBMITTED BY R. N. MAXSON*
CHECKED BY H. S. BOOTH† AND C. V. HERRMANN†

Procedure

The dried silver residue is treated with aqua regia (**Care!** Hood!). After action has ceased the solution is filtered through glass wool and the residue is washed to

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† Western Reserve University, Cleveland, Ohio.

remove any soluble materials.* This treatment should remove lead, mercury, and the other common metals. The precipitate of silver chloride is then dissolved in the least possible amount of concentrated ammonium hydroxide (sp. gr. 0.90). This solution is filtered to remove insoluble impurities, cautiously treated with dilute nitric acid (6N) until definitely acid, and heated to coagulate the precipitated silver chloride. The precipitate is washed by decantation until the washings are neutral to litmus.

The silver chloride is transferred to a casserole, covered completely with concentrated hydrochloric acid, and stick zinc of high purity is added to reduce the silver to the elemental form. The metal is washed thoroughly with water until the last washings give no test for the chloride ion.

The metal is dissolved in dilute nitric acid (1 volume concentrated acid to 1 volume water). A large volume of distilled water is added, and the solution is permitted to stand for at least 12 hours. Tin, antimony, and bismuth, if present, are precipitated here.

The solution is filtered, and the silver precipitated again by the addition of a small excess of concentrated hydrochloric acid. After heating carefully on a water bath, the supernatant liquid is decanted. Dilute hydrochloric acid (6N) is added to the residue, and the mixture stirred thoroughly. The precipitate is allowed to settle, and the supernatant liquid is again decanted. This treatment is repeated several times, and the silver chloride is finally filtered off and washed with water until the last washings give no test for the chloride ion.† The residue is again treated with concentrated hydrochloric acid and zinc. The metallic silver is washed free from chlorides and weighed while moist.

* If the residue is not badly contaminated, the dry material should be treated with ammonium hydroxide and filtered. The filtrate is acidified with nitric acid, and the precipitated silver chloride treated as specified in the procedure.

† The washings should also give a negative test for the cupric ion.

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The silver is dissolved in dilute (7.5 N) nitric acid. An excess of 20 per cent above the calculated weight of formic acid (85 per cent) needed for reduction* to metallic silver is neutralized with a slight excess of ammonium hydroxide, and the resultant solution added drop by drop to the hot silver nitrate solution. The granular precipitate of silver is washed with hot water and dried by suction or between filter papers.

* A definite excess of nitric acid must be present during this reduction.

CHAPTER II

3. PREPARATION OF AMALGAMS

By L. F. Audrieth*

Introduction

An amalgam may be defined as a liquid or solid alloy one of whose components is mercury. Amalgams may consist of either liquid or solid solutions of metals in mercury, or they may be definite intermetallic compounds, such as LiHg, $NaHg_2$, $CsHg_4$.[1] The ability of various metals to form amalgams varies considerably. Elements that are chemically similar to mercury and in close proximity to it in the periodic table amalgamate readily. Elements with high melting points form amalgams with difficulty. Furthermore, if a metal is not wet by mercury there will be little opportunity for combination to take place unless it is effected under conditions where the mercury comes in contact with the metal in an active condition.

The solubilities of various metals in mercury at 18° C. are noted in the accompanying table. Concentration of the saturated amalgam usually results in the precipitation of the dissolved solute as a mercuride, rarely in the form of the free metal. It should be noted that metals chemically and physically similar to mercury are characterized by high solubility. The farther removed in the Mendeléev periodic table the metals are from mercury the less soluble they become. Actually none of the metals except thallium is extremely soluble; consequently, methods leading to the preparation of amalgams often give products

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that are heterogeneous in nature. In the case of a pasty or semisolid amalgam, the crystalline material may readily be separated from the saturated solution of the metal in liquid mercury by filtration through a chamois skin. In many instances, it is possible to concentrate amalgams with respect to their metal content by heating under reduced pressure. In fact, it has been found possible to eliminate the mercury completely from an amalgam by high-temperature vacuum distillation. This method has been utilized with success in the preparation of barium, neodymium, lanthanum, and cerium.[2]

SOLUBILITY OF METALS IN MERCURY AT 18°[3]
(In percentage by weight)

Li	0.09	Mg	0.24	Sn	0.62
Na	0.68	Ca	0 30	Bi	1.4
K	0.80	Ba	0.33	Cr	3.1×10^{-11}
Rb	1.54	Zn	2.15	Mn	2.5×10^{-4}
Cs	4.34	Cd	4.92	Fe	1.0×10^{-17}
Cu	3.2×10^{-3}	Tl	42.8	Ni	5.9×10^{-4}
Ag	4.2×10^{-2}	Pb	1 3	Co	1.7×10^{-1}
Au	1.3×10^{-1}				

Various methods have been employed for the preparation of amalgams.[4] Each has certain advantages, and each is especially applicable in certain cases. They may be grouped into four general classes:

1. Direct combination.
2. Electrolysis of a solution containing the metallic ion using a mercury cathode either in
   a. Aqueous solutions, or in
   b. Non-aqueous solutions.
3. Displacement of an ion from either aqueous or non-aqueous solution by a more active amalgam.
4. Displacement reactions involving the action of
   a. An active metal upon a solution of a mercuric salt.
   b. Mercury upon a solution of a salt of a more noble metal.

The first three are illustrated by specific examples in the syntheses that follow. Sodium amalgam (synthesis 4) is readily prepared by direct combination of the metal with mercury (illustrating method 1). Barium amalgam (synthesis 5) can be produced readily by the electrolysis of a saturated aqueous solution of barium chloride with a mercury cathode (illustrating method 2*a*). Barium amalgam is also easily obtainable by the action of sodium amalgam upon a concentrated aqueous solution of barium chloride (illustrating method 3).

Methods of direct combination are especially desirable in those cases where the metal to be amalgamated is readily available. It is generally necessary to heat the two constituents together to effect solution and reaction. Where either the metal or the product is reactive, the preparation is carried out under an inert solvent, in an atmosphere of hydrogen or nitrogen, or by heating in a vacuum in a sealed glass tube or metal bomb.

Many metals can be discharged at a mercury cathode, because of its high hydrogen overvoltage. Electrolytic methods for the preparation of amalgams have therefore been widely used and are especially advantageous, since intimate contact of mercury with the discharged metal is thereby effected. It may be assumed that the amalgamation process is a rapid one under these circumstances, because of the fact that the metal is in the active atomic state at the moment of its discharge from the ionic form. In using the electrolytic method, it is generally desirable to employ rather concentrated solutions in order that the reverse reaction of decomposition of the amalgam by the solvent may be reduced to a minimum. Furthermore, salts containing anions that are easily reduced, such as the nitrate, should not be used.

The electrolytic method is especially useful in those cases where the metals are not readily obtainable in the free state or where they are too active to permit use of the method of direct combination. Potassium, rubidium,

and cesium amalgams are obtained from solutions of the corresponding hydroxides; barium and strontium amalgams, from solutions of the chlorides.

The electrolytic method has also been applied in several cases where direct combination is not very successful because of the high melting points of the metals. Chromium amalgam has been obtained by the electrolysis of a concentrated aqueous solution of chromic chloride strongly acidified with hydrochloric acid; molybdenum amalgam, from acid solutions of the trioxide. This method has also been employed for the preparation of amalgams of such common metals as zinc, lead, cadmium, tin, bismuth, and manganese. Amalgams of aluminum, calcium, magnesium, and beryllium have not yet been obtained by the electrolysis of aqueous salt solutions.

A modification of the electrolytic method involves the electrolysis of solutions containing both the metallic and the mercuric ions. This procedure should possibly lead to the deposition of amalgams of varying composition, but no extensive study of this sort has ever been reported. Bismuth and copper amalgams have been prepared in this manner.

In some instances, non-aqueous solvents can be used to advantage, and many examples of electrodeposition from solutions of salts in solvents other than water have been reported.[5] Electrolysis of aqueous solutions of rare earth metal chlorides at a mercury cathode results in the formation of amalgams, but at the same time a considerable quantity of basic salt precipitates which is difficult to separate. While alcoholic solutions of the chlorides are marked by a much higher resistivity to the electric current, the amalgams can be obtained from them without difficulty. Amalgams of tetramethylammonium[6] and its higher analogs are also obtainable by electrolysis of the corresponding chlorides in alcoholic solutions at $-34°$. Electrolysis of ammonium thiocyanate in acetone using a mercury cathode is said to yield ammonium amalgam.[7] It is

claimed that a very concentrated barium amalgam containing up to 30 per cent barium may be prepared by the electrolysis of barium iodide in pyridine.[8]

Where absolute purity is not required amalgams can be prepared by the action of an active amalgam, such as sodium amalgam, upon an aqueous or non-aqueous solution of a metallic salt. It is usually somewhat difficult to achieve complete reaction and the final product will always contain traces of the reacting amalgam (see the table). The method is a very simple one, especially since sodium amalgam is easily prepared. Ammonium, barium, strontium, and chromium amalgams have been prepared in this manner. Recently the rare earth metal amalgams have been prepared by the action of sodium amalgam on alcoholic solutions of the chlorides.[9] This reaction does not take place in aqueous solution. Apparently the reaction is aided in alcohol because of the fact that sodium chloride is insoluble and precipitated from solution, thereby driving the reaction to completion as follows:

$$3NaHg_x + NdCl_3 \xrightarrow{\text{in } C_2H_5OH} 3NaCl\downarrow + NdHg_x$$

The fourth method finds limited application, although amalgamated metallic surfaces are readily prepared by dipping the metal into a solution of a mercuric salt. An illustration of the action of mercury on the solution of a salt of a more noble metal is to be found in the preparation of the silver mercuride, Ag_3Hg_4.[10] The addition of drops of mercury to a solution of silver nitrate yields crystals of this intermetallic compound.

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4. For general discussions on the subject of amalgams see (*a*) Friend: "A Textbook of Inorganic Chemistry," Vol. III, Part II, p. 215, Charles Griffin & Company, Ltd., London, 1926; (*b*) Mellor: "A

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