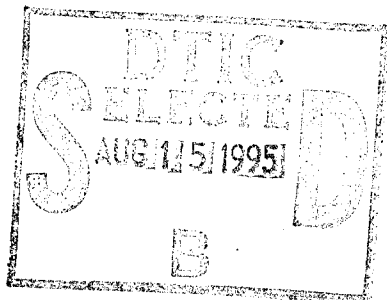


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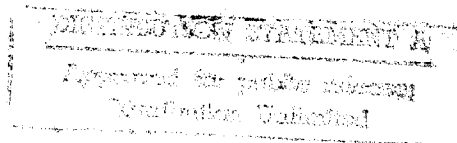
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UNITED STATES ATOMIC ENERGY COMMISSION

THE REACTION OF ORGANOSODIUM
COMPOUNDS WITH URANIUM TRIBROMIDE
(WITH STUDIES ON THE NATURE AND
SEPARATION OF REACTION PRODUCTS)

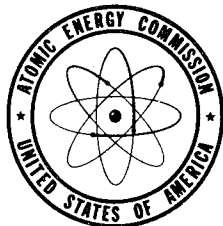
Annual Report for Year Ending June 1, 1954

By
Thomas R. P. Gibb, Jr.
Edward J. Goon
Edwin B. Damon



June 15, 1954

Tufts College
Medford, Massachusetts



Technical Information Service, Oak Ridge, Tennessee

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TUFTS COLLEGE

Annual Report

NYO-3916

THE REACTION OF ORGANOSODIUM
COMPOUNDS WITH URANIUM TRIBROMIDE

(With Studies on the Nature and Separation of Reaction Products)

By

Thomas R. P. Gibb, Jr.

Edward J. Goon

Edwin B. Damon

with the assistance of

Robert Barry
Mary C. Ciampa

(This report covers one phase of research under Contract AT(30-1)1355. Work on the thermodynamic evaluation of preparative reactions is given in NYO-3913; the dissociation of UH_3 in NYO-3914 and transition metal hydrides in NYO-3917.)

For Year Ending June 1, 1954

TUFTS COLLEGE

Work performed under Contract No. AT(30-1)1355.

Issued June 15, 1954

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ABSTRACT

The reaction of sodium in biphenyl, amylsodium, sodium benzophenone ketyl, and sodium naphthalene glycol ether with uranium tribromide is reported. Evidence is given that colloidal uranium is formed in certain instances but is too reactive to be isolated except in partially oxidized form. Reduction by organosodium reagents in the presence of hydrogen gas does not lead to uranium hydride in the reactions studied. Various observations on the reactivity of finely divided uranium and uranium tribromide with possible leaching agents are described. Uranium powder reacts with water, dilute base, isopropyl alcohol and, to some extent, with ether-methanol and acetone, but not with liquid ammonia. Uranium tribromide reacts with isopropyl alcohol and sodium isopropoxide forming isopropylates and with liquid ammonia probably to form the insoluble triamide. The density and x-ray diffraction pattern of uranium hydride as a function of hydrogen content have been measured, and a preliminary report is given indicating partial removal of H at low temperature does not greatly increase the density above that of UH_3 .

A special drybox and certain anaerobic techniques are described together with a microscope hot-stage for observations in vacuum or under high gas pressures.

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SUMMARY

This report taken together with NYO-3913, NYO-3914 and NYO-3917 constitutes an annual report of work under Contract AT(30-1)1355. Included herein is a full description of studies on the low temperature reaction of UBr_3 (and UF_4) with various organosodium compounds in a hydrogen or in an argon atmosphere, and with sodium sand in biphenyl at $250^\circ C$. These reactions were studied as a possible route to the preparation of powdered metal from uranium salts. The pertinent chemistry of several organosodium compounds is discussed. Also reported is a series of investigations on the reactions of uranium and uranium tribromide with solvents proposed as leaching agents. This report includes a study of the relation of the density of the solid phase of the U- H_2 system as a function of hydrogen content. In the last sections of the report various techniques and special items of equipment are described.

Uranium tetrafluoride was found not to react with amylsodium but UBr_3 was reduced by the latter reagent to unidentified products. Hydrogen was not absorbed by amylsodium or by the reaction mixture. The sodium ketyl of benzophenone was found to react with UBr_3 presumably to form an extremely active colloidal or nearly colloidal uranium metal. This metal or black product could not be isolated in pure form but in a partially oxidized form which reacted with dilute acid giving hydrogen, burned in air and was substantially free of bromide. It was accompanied by NaBr. When the UBr_3 -ketyl reaction was carried out under hydrogen no absorption of the latter was observed.

Uranium tribromide reacts with a solution of sodium naphthalene in dimethyl cellosolve yielding a mixture of products including a dense black pyrophoric material which may be colloidal uranium. No satisfactory method of isolating this was found.

Sodium sand in biphenyl was found to react smoothly but incompletely with uranium tribromide at $250^\circ C$. Considerable amounts of NaBr were obtained together with an extremely reactive fine black powder similar to that observed in the above-mentioned reactions.

In view of the difficulty experienced in isolating products, further studies of preparative reactions were postponed until separatory techniques could be worked out. This proved to be a most difficult undertaking for it was found that pure finely divided uranium, contrary to the consensus of other workers, reacts with water, methanol, isopropyl alcohol, aqueous alcohols, dilute aqueous NaOH and, to some extent, with acetone. The problem of separating uranium from sodium halide by leaching requires that the leach dissolve the sodium halide without reacting with the uranium. So far only liquid ammonia has been found to fulfill this requirement.

Summary Con't.

Liquid ammonia does not react with finely divided uranium, and gaseous ammonia appears not to react appreciably up to 100°C. Unfortunately liquid ammonia reacts with UBr_3 and probably all lower uranium halides to form an insoluble material which is extremely difficult to filter. Since uranium halide is a likely constituent in the mixtures to be separated, liquid ammonia is not a satisfactory leaching agent, even though it is the best tried to date. The reaction product of liquid ammonia with UBr_3 appears to be an ammoniated amide, presumably $U(NH_2)_3 \cdot 3NH_3$ rather than $UBr_3 \cdot 6NH_3$ as reported in the literature. This formulation is provisional and additional evidence is needed.

Isopropyl alcohol not only reacts with uranium but also with uranium tribromide forming uranium bromide isopropoxides. Sodium isopropoxide reacts with UBr_3 forming uranium trisopropoxide which is apparently a new compound. These alcoholates are readily hydrolyzed. Leaching of the partial reduction product of UBr_3 and sodium or organosodium compounds with isopropyl alcohol thus leads to substances which are readily hydrolyzed to uranium oxides. This undoubtedly accounts for the presence of UO_2 in some of the reduction products leached with isopropyl alcohol.

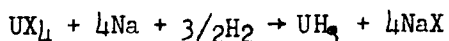
The reduction of uranium salts by sodium or organosodium compounds in the presence of hydrogen to form UH_3 was considered both likely and desirable because of thermodynamic calculations. (NYO-3913) The evidence obtained with amylsodium at 10°C and sodium sand in biphenyl at 250°C indicates that the rate of absorption of hydrogen is negligible.

A parallel study is in progress of the properties of uranium hydride. Present evidence shows that approximately one atom of hydrogen may be pulled out of UH_3 at low temperature (in vacuum) without causing formation of a uranium phase and with relatively little change in the density. This indicates that the UH_3 lattice is preserved with vacancies where some of the hydrogen atoms have been removed. Such work, if confirmed, is of considerable theoretical and practical interest.

Brief descriptions are given of a novel apparatus for carrying out small-scale reactions, filtrations and extractions anaerobically; a large drybox and gas-purification systems and a microscope hot-stage for use in studying the U- H_2 interaction, etc. at high hydrogen pressures or in vacuum. A brief description is given of a technique for determining hydrogen and carbon in pyrophoric or air-sensitive samples by combustion.

1.00 INTRODUCTION

This report describes the results obtained in a series of exploratory surveys whose original objective was to find a method of preparing uranium hydride or uranium in finely divided form. These preparative studies were preceded and guided by a review of the thermodynamic feasibility of various selected low-temperature reactions. (1) The review strongly indicated the desirability of using sodium for the reduction of uranium chloride or bromide in the presence of hydrogen:



This reaction, and indeed any similar reaction leading to UH_3 must be conducted at temperatures well below the usual metallurgical range owing to the dissociation of the hydride above ca $350^\circ C$. (2) As written, this reaction has a favorable free energy ($-\Delta H$) of 156.9 Kcal at $25^\circ C$ and 142.8 Kcal at $227^\circ C$ for UCl_4 .

In view of these large energies it may be assumed that once started such a reaction should be quite exothermic and rapid. This is indeed the case, as we have shown on a prudently small scale. To start the reaction requires heating to somewhat above the melting point of sodium (ca $90^\circ C$) but unless subsequently heated to much higher temperature it apparently does not go to completion. At these higher temperatures the economy and simplicity of the method as well as the favorable energy balance are largely lost. Indeed the reaction of sodium with UCl_4 described in 1869 by Peligot (3) has never merited widespread attention for this reason.

Accordingly, we considered three ways in which this reaction might be utilized to advantage. These were:

a) Electrolytic generation of the sodium in a low-melting salt bath containing uranium halide.

b) Carrying out the reaction in the presence of an inert liquid which would act as a coolant and also maintain a clean reactive surface on the sodium at ca. $200-350^\circ C$.

c) Carrying out the reaction as in b) but at a somewhat lower temperature in the presence of an unstable organometallic compound of sodium, the organic moiety serving simply as a carrier of sodium.

The first of these ways has not yet been attempted in this laboratory since closely related work was well advanced elsewhere. The second is still being studied by us and will be reported in due course. The third approach is reported at this time although it has by no means been entirely explored.

During the course of the work it became clear that three side issues would have to take precedence over the principal objective. The most critical of these was the need for a survey of the reactivity of uranium towards various organic and inorganic liquids and solutions.

While it appears likely that some of our early reactions led to colloidal metal, the methods of separation tried always resulted in loss of the entire product. In this earlier work isopropyl alcohol both anhydrous and aqueous and pure water were used for the removal of sodium bromide and other by-products. Since uranium oxide UO_2 was always the product, it was suspected that the uranium was attacked by these reagents. This indeed was evidently the case, for colloidal uranium prepared by degassing the hydride was found to react rather rapidly with both air-free water and alcohols at room temperature contrary to some reported data for massive metal (4). A study was made therefore of the reactivity of uranium with various possible leaching agents and is reported in a subsequent section.

The second side-issue which required attention was the behavior of these possible leaching agents with expected products and reactants such as sodium, UBr_3 , $NaBr$, etc. A successful leaching agent should remove all undesired materials from the uranium. If the leaching agent fails to remove such or if it enters into or causes a reaction leading to an insoluble product, this fact must be established. Isopropyl alcohol for example largely dissolves UBr_3 , but if sodium accompanies the UBr_3 , as is likely in the above-mentioned reductions, an insoluble or sparingly soluble material approximating $UBr_2(OPr)$ is formed. In the same way liquid ammonia which is inert towards uranium and an excellent solvent for sodium and $NaBr$, reacts with UBr_3 to form an insoluble amide.

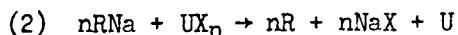
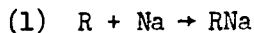
The third preliminary investigation was concerned with the solubility of uranium halides in hydrocarbon or ether solvents which would be inert towards sodium. Almost no data are available on this subject. A somewhat cursory survey was conducted which revealed no promising leads, the number of likely liquids being considerably diminished by the drastic requirement that these should be polar with a high dielectric constant and yet unreactive with sodium. (Since oxygen may not be present in the reducible uranium compound, such hydrocarbon soluble compounds as the alkoxides are ruled out.)

These preliminaries are themselves a sufficient research challenge because of the extreme sensitivity of most of the materials towards air and traces of impurities. A whole technique of anaerobic manipulation had to be devised, methods of extreme drying of inert gases, etc. etc. Some of these techniques which appear of broad utility are described under the heading "Special Apparatus and Techniques" or in relevant portions of the text. We are of the opinion that the organosodium reduction problem is now at the stage where its inherent complexity is clearly established and that any continuation should not be based on its probable utility as a method of producing uranium, but frankly on the basic knowledge of the unusual compounds and chemistry involved.

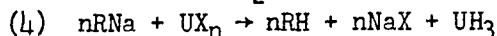
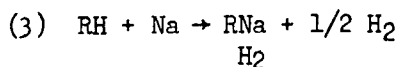
The general and detailed account of the organo-sodium reductions and leaching studies are contained in the following sections. An account of our dissociation studies on uranium hydride is given in an earlier topical report NYO-3914. The work on microscopic examination of the formation and dissociation of uranium hydride by means of a special hot-stage is to be described in a future report. The design of this hot-stage is given in the section on special apparatus.

1.10 General Survey of Applicable Organo-Sodium Compounds

The only type of organo-sodium compound likely to be economically feasible as a reducing agent for production of uranium must obviously be formed readily from metallic sodium. The organic portion must also be regenerated by reaction with the uranium compound so that the net function is that of a sodium carrier, e.g.:



or possibly:



where R represents the organic carrier and X halogen.

Various alternatives involving RX as an intermediate may be discounted, although the presence of RX or RR, etc. as a side-product should not be ignored. In either of the above reactions UR_n or UR_xX_y may be involved. Presumably the uranium-carbon bond in this type of compound is extremely labile. (5) Notwithstanding the evident existence of the somewhat analogous Ti-C bond in such compounds as $C_6H_5Ti(OC_2H_5)_3$ (6) it is highly unlikely that an organo-uranium compound will be other than transitory. Indeed Gilman (7) has shown that phenylthallium decomposes to the free metal and has cited indications by other workers that titanium is formed by decomposition of the reaction product of $TiCl_4$ with zinc diethyl. (8)

Reaction (1) implies an addition of sodium to an unsaturated molecule R. Many organic molecules show this type of addition e.g. ketones devoid of alpha hydrogens such as benzophenone; (9) polycyclic condensed ring hydrocarbons (especially in the presence of activating solvents such as cellosolve ethers); (10) polyaryl substituted ethylenes, (11) (even styrene to a limited extent), stilbene, benzal aniline, (11) pyridine, etc. (12)

In the majority of cases, highly colored extremely reactive mono or di-sodium compounds are formed by these substances which with few exceptions regenerate the organic precursor on reaction with non-hydroxylic reagents. Many, if not most of these substances are reducible by hydrogen although not readily. It is possible that reaction (1) could be conducted under hydrogen without hydrogenation of the organic carrier, but the presence of colloidal U or UH_3 might be expected to catalyze such hydrogenation. Nevertheless, some of these unsaturated molecules add sodium more readily than they add hydrogen to form a saturated product. Thus, the di and triphenyl ethylenes add sodium very easily to form free radicals written in dimeric form as e. g.: - $(C_6H_5)_2 C (Na) C (Na) (C_6H_5)_2$.

If the original ethylenic double bond were to be reduced, the tetraphenylethane resulting would react by substitution with sodium presumably forming the same disodium compound. In this case then, hydrogen would have no net effect on the use of tetraphenylethylene as a carrier. No attempt was made in this work to ascertain whether a hydrogen atmosphere could be used in this type of reaction.

Reaction (2) above-mentioned represents a facile substitution of hydrogen attached to an organic molecule, by sodium. Such a reaction would be especially advantageous for the production of UH_2 since the organic molecule need not be unsaturated. Molecules of the type of triphenyl methane, tetraphenylethane, fluorene, benzthiophene, etc. are familiar examples of this type of substitution by sodium. Unfortunately in most instances the heat of formation of the sodio compound is quite significant (see section on heats of formation). Therefore some of these carriers of sodium are rather more stable or less reactive than the additive-type carriers. In this work no substitutive type carriers have been investigated for this reason although it may be supposed that at temperatures where they are in equilibrium with sodium they should be operative.

A model of a substitutive organo-sodium compound was used in our study of the UBr_3 reduction. This model, n-amylsodium $\text{C}_5\text{H}_{11}\text{Na}$ is not regenerative i.e. n-pentane does not react with sodium, but it was chosen because it is a familiar, easily prepared and very reactive material. (13) Moreover, amylsodium is capable of metallating many organic molecules such as benzene, toluene, fluorene, triphenylmethane, etc. Therefore, it seems reasonable to suppose that amylsodium is one of the most reactive organo-sodium compounds and that if it does not effect reduction of UX_3 or UX_2 then there is little chance that phenylsodium, benzyl-sodium, etc. will do so either. This reasoning is open to the objection that the ability of amylsodium to metallate, e.g. toluene, is more a function of the acid strength of pentane relative to that of toluene than of the reducing power of the two sodio compounds. Nevertheless, there must be a rough parallelism between K_A and reducing power, allowing for such divergencies as may be caused by differences in solubility, colloidal behavior, etc.

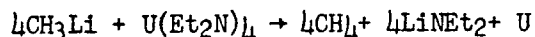
Our observation that amylsodium did not react with UF_4 resulted in the perhaps unwarranted elimination of this fluoride from subsequent trials. Amylsodium did however react with UBr_3 as discussed in the appropriate section below. The lack of solubility of amylsodium in the solvents necessarily employed and its thermal decomposition above ca 25°C rendered it less suitable as a model reducing agent than was originally hoped.

1.20 Corresponding Behavior of Organo-Lithium Compounds

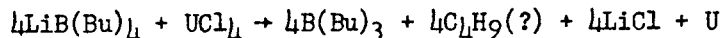
Organo-lithium compounds are in many respects quite different from organo-sodium compounds and are generally more soluble and less reactive towards replaceable halogen. Lithium is thermodynamically inferior to sodium for the re-

duction of $U\text{Br}_3$ or $U\text{Br}_4$, but it is possible that this is not always true for the corresponding organometallic compounds.

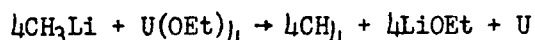
Gilman has reported (14) that the diethyl amide of tetravalent uranium $U(\text{Et}_2\text{N})_4$ is reducible by methyl-lithium in ether solution to what appears to be metallic uranium.



The black product was not isolated however. Lithium tetrabutylborate $\text{LiB}(\text{Bu})_4$ readily reduces uranium tetrachloride in ether to a black pyrophoric solid believed by Gilman to be uranium metal (but which may have been a novel boride):



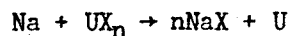
More pertinent is Gilman's further observation that uranium tetroxide in ether solution is reduced by methyl-lithium to uranium metal:



This and the foregoing reactions are claimed to take place at room temperature. The uranium presumably produced could not be isolated and analyzed. The above equation is obviously not balanced and it may be assumed that instead of 4 mols of methane actually two mols accompanied by one mol of ethylene may have been meant. If measured volumetrically this would approximately account for the 73% yield of "methane" actually observed. Any succeeding reports on this subject were not available.

1.30 Some Considerations on the Stability, Solubility and Reactivity of Organosodium Compounds.

In addition to those properties considered in the preceding paragraph, an organosodium compound suitable for the purpose of sodium-carrier should have a low heat of formation and a low free energy of formation. It is evident that the desirable heat and free energy balance of the reaction



will be made less favorable if the sodium is replaced by an organosodium compound having a high heat or free energy of formation. On the other hand, if the organosodium compound has a free energy of formation close to zero, it may not form with sufficient readiness or in sufficient quantity.

Amylsodium, used as a model substance evidently has a free energy of formation close to zero at room temperature since it decomposes slowly to give sodium and what is probably a mixture of pentene, decane and other hydrocarbons. Therefore, it should be a more aggressive reducing agent than, say triphenylmethylsodium which is not as labile.

Indeed, the free energy of formation of the latter (in ether solution) amounts to -17.9 Kcal per mol. (15) This value, and certainly the free energy of formation of most organosodium compounds considered here will be profoundly affected by the solvent. The free energy of solvation of the sodium ion is reported by Bent as roughly 70 to 77 Kcal. per mol for solutions of triphenylmethyl sodium in ether.

If the free energy of solvation of sodium ion (so-called) is of this magnitude, there is an implication that the high observed free energy of formation of some organosodium compounds (e.g. triphenylmethylsodium) is due largely to solvation rather than to the stability of the C-Na bond. Consequently, it may be that homogeneous solutions of organosodium compounds should be replaced in this work by suspensions in inert solvents. This has indeed been done in our work and not entirely by choice, for the reaction conditions and the reactivity of the species employed are such that hydrocarbon media are generally necessary. We have obtained no evidence of solubility in these media of the organosodium compounds or uranium halides tested.

The possibility that most organosodium compounds will react in a hydrogen atmosphere to form sodium hydride and a saturated organic compound was considered. It appears that while this reaction can take place at high temperature (16) we have found no evidence that it is an interfering factor under the conditions we have employed for the reaction of UBr_3 etc. with amylsodium, sodium benzophenone ketyl and sodium dispersions in biphenyl.

No evidence is available on the heat of activation of reactions involving organosodium compounds. Neither the rate of formation nor the rate of reaction with analogous halides has been studied. The rate at which sodium adds to benzophenone, tetraphenylethylene, etc. is very rapid and presumably depends, in the practical sense at least, on the available surface of the sodium.

The rate at which insoluble organosodium compounds will react with insoluble uranium salts is almost certainly dependent on the degree of contact between particles. This depends on the fineness of subdivision and the absence of protective layers on the particles. The rate of solid state diffusion at the surface and within these particles is also of importance but is difficult to evaluate or control. The surface area of the organosodium reagents is evidently very large since these are formed as almost gelatinous suspensions. The particle size of the uranium salt is reduced progressively during reaction by the high speed stirrer employed (17) which also aids in the removal of protective layers (e.g. of NaBr). The rapid change in color accompanying most of our reactions between UX_n and organosodium compounds is evidence of the speed of at least the first step of the reaction.

It would certainly be desirable to produce the uranium salt in colloidal form prior to reduction, or preferably to employ an inert solvent which would dissolve all or any of the reactants and intermediates. Unfortunately, no liquid has been found to possess the necessary properties and it seems certain that reactions such as those described will have to be heterogeneous.

2.00 ~~THE~~ REACTION OF AMYLSODIUM WITH $U\text{Br}_3$ and UF_4 . (M.C.Ciampa)

2.10 General Description

As noted in the introduction amylsodium $C_5H_{11}Na$ was selected as the first organo sodium compound to be tried because it is one of the more powerful and familiar reagents. It is not a carrier-type reducing agent and may not be used much above 10°C . Its reactions with $U\text{Br}_3$ and UF_4 in argon and hydrogen atmosphere were studied briefly.

2.20 Preparation of Amylsodium

The reagent was prepared by adding amyl chloride or bromide to sodium sand suspended in chilled heptane according to the technique of Morton et al.(39) The deep bluish-purple amylsodium was formed ordinarily in about 80% yield based on amyl halide, as shown by carbonation and estimation of total carboxylic acids. In some runs di-n-butyl ether was added to the amylsodium with which it does not appear to react. (60-70% yields of amylsodium were noted in the presence of the ether)

2.30 Preliminary Test of Reduction of $FeCl_3$

Owing to a delay in the procurement of U or U halides cursory tests were run on the reduction of $FeCl_3$ by amylsodium in n-butyl ether. These test runs were largely for the purpose of becoming familiar with the technique. When a solution of $FeCl_3$, anhydrous in di-n-butyl ether was added to an equivalent amount of amylsodium in heptane, the blue color of the amylsodium was instantly replaced by a dark red-brown color which became almost black. Qualitative tests indicated a ferrous compound but a powerful magnet had no apparent effect on the suspension. The nature of the pasty brown material was not ascertained. On carbonation in the presence of isopropyl alcohol a pasty brown mass and reddish-brown filtrate resulted.

2.40 Preliminary Test of Reduction of UF_4

Since UF_4 is more easily handled than the hygroscopic halides, it was tested first. An attempt was made to find a solvent for this salt which would be inert towards amylsodium. No solubility of UF_4 in hydrocarbons, di-n-butyl ether, benzotrifluoride, bis(trifluoromethyl) benzene or perfluoromethylcyclohexane could be observed. A suspension of UF_4 in heptane-di-n-butyl ether was added to amylsodium at 10°C and the mixture stirred overnight at room temperature. No evidence of a reaction was noted. The purple amylsodium color was unaffected. The mixture was decomposed with n-butyl alcohol and the characteristic light green color of UF_4 was observed. A small amount of black material was present but did not bubble when acidified with HCl.

2.50 Reaction of $U\text{Br}_3$ with Amylsodium

Several runs were carried out by addition of powdered $U\text{Br}_3$ (prepared from UH_3 and HBr) to a 10-20% excess of amylsodium in heptane and heptane-di-n-butyl ether under argon or hydrogen. In all cases addition of the $U\text{Br}_3$ to the

amylsodium at 0-10°C resulted in an immediate color change from blue to brown. In those reactions under hydrogen no hydrogen was absorbed (within the rather large experimental limits) although in one case a small volume of hydrogen may have been absorbed by amylsodium prior to addition of the $U\text{Br}_3$. The $U\text{Br}_3$ contained some $U\text{Br}_4$ as evidenced by the color and composition ($U\text{Er}_3.48$ reported by the New Brunswick Laboratory).*

The brown reaction mixture was left for 24-72 hours at room temperature and filtered under reasonably anaerobic conditions. The solid dark product was leached with naphthalene-glycol ether reagent (see section 4) to remove sodium (and the completeness of its removal checked by the color imparted to liquid ammonia by a small sample of the leached solid). The sodium-free solid was washed with aqueous isopropyl alcohol to remove $U\text{Br}_3$, NaCl , NaBr and the very small amount of resulting black solid examined by x-ray diffraction. (Washken Laboratories, Cambridge, Mass.) The x-ray work was not useful however and there is some doubt that the consulting laboratory's equipment was operating satisfactorily.

This preliminary work was carried out before it was realized that finely divided uranium would react with aqueous isopropyl alcohol, and it is likely that the product was largely lost due to this reaction. The work afforded evidence that $U\text{Br}_3$ reacted with amylsodium but the intractability of the products, the long reaction time and the necessarily low temperature suggested that this reaction was not useful even as a model.

*We have as yet been unable to obtain a correct analysis for $U\text{Br}_3$ prepared by the method recommended by Katz and Rabinowitch.

3.00 REACTION OF URANIUM TRIBROMIDE WITH SODIUM BENZOPHENONE KETYL

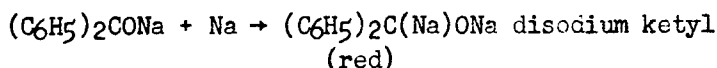
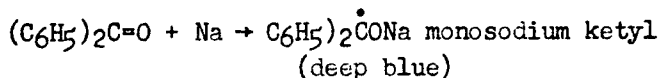
As noted earlier, the sodium addition compounds formed by ketones and known as "ketyls" are powerful reducing agents at ordinary temperatures. Moreover, when so used these ketyls usually regenerate the original ketone. Thus, the latter serves simply as an activator or carrier of sodium, permitting room-temperature reductions not possible with metallic sodium itself.

3.10 General Discussion of Ketyls and Their Preparation

The following treatment deals only with the sodium compounds formed by benzophenone since this system is the only one investigated at length. It should be kept in mind however that all of the alkali metals, with the usual exception of lithium, form ketyls, and that most ketones which do not contain α -hydrogen atoms may form ketyls. The "ammonium metal" analogs are also known.

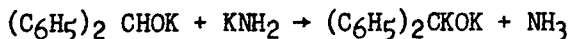
The ketyls are generally made by reacting molten sodium or sodium sand with the ketone in ether. The presence of ether was once thought essential (18) but is evidently not although it undoubtedly promotes the reaction owing to its solvent or complex forming properties.

According to Schlenk and co-workers (19) who have studied the reaction most thoroughly, the sodium adds stepwise to the carbonyl double bond:



The monosodium ketyl is almost certainly a free radical $(C_6H_5)_2\dot{C}ONa \leftrightarrow (C_6H_5)_2CONa$. since its magnetic susceptibility is only slightly less ($\mu = 1.45$) than that associated with a postulated free radical with one electron ($\mu = 1.73$). (20) The disodium compound forms with less ease, and in the absence of ether temperatures of ca 100°C or prolonged stirring are required. It is also presumed to be a free radical although Hantzsch (21) has argued its ionic character $Na^+(NaOC(C_6H_5)_2)^-$. It separates as a deep red precipitate from the solution or suspension of blue monosodium compound.

Solutions of sodium in liquid ammonia react readily with benzophenone forming the ketyls. (22) In this solvent, the dipotassium ketyl may be prepared by the reaction of an alcoholate with potassium amide:



This preparation is presumably an equilibrium reaction which argues for the ketyl a rather lower reducing power than assumed above. This inference is corroborated by the alleged preparation of the monosodium ketyl from benzophenone: (23)



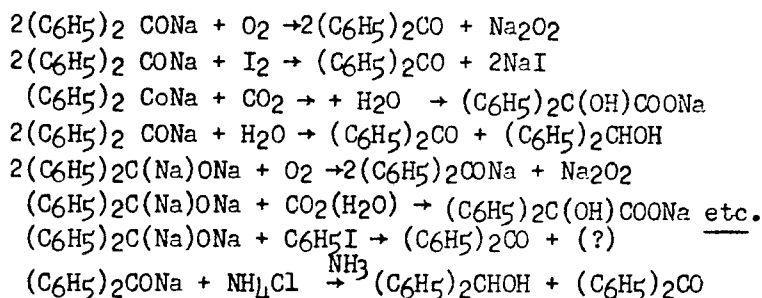
It is also claimed that sodium amalgam reduces benzpinacolone (benzopinacolone) to the monosodium ketyl. The former reaction evidently requires further study.

The following additional references apply to the preparation and general properties of ketyls:

- Wooster (Review of Alkali Metal Organometallic Compounds) Chem.Rev.11,1(1932)
 Gilman (Survey of Organometallic Compounds) "Organic Chemistry" Vol. I p 526
 2nd Ed. John Wiley and Sons, N.Y. 1943
 Kraus and Bien (Liquid Ammonia Studies) J.Am.Chem.Soc. 55, 3612(1933)
 Schlubach (Liquid Ammonia Studies) Ber. 48, 12(1915)

3.20 Properties and Reactions of Ketyls

The ketyls are powerful reducing agents reacting almost instantly and presumably by addition with gaseous oxygen at room temperature, with sulfur, iodine, carbon dioxide, water, etc. as indicated below. The disodium ketyl appears to react in stepwise fashion, via the monosodium compound although the evidence for this is largely the observed color change.



In common with most other sodium 1-2 addition compounds, benzophenone tends to be regenerated by reaction with oxidizable substances. Water and carbon dioxide are the only cited reagents which fail to regenerate the original ketone. So far as known there appears to be no literature bearing on the reaction of ketyls with reducible metal compounds. It may be predicted, however, that the latter would tend to regenerate benzophenone unless a side reaction occurred. (See following section on properties of benzophenone).

These ketyls are soluble in liquid ammonia and in diethyl ether.

3.30 Reactions of Benzophenone

Pure benzophenone may be heated to 650°C in the absence of air without decomposition. A copper or chrome-vanadium bomb was used for the tests. It is thus extremely stable towards heat.

If benzophenone is to be used solely as a sodium carrier it obviously must not react with any of the substances present in the UX_3-Na-H_2 system. The reduction of benzophenone by hydrogen has been reported. It is reduced by hydrogen under conventional pressures in the presence of platinum black at room temperature to give diphenyl-carbinol and ultimately dyphenylmethane in good yield. (24) With nickel oxide catalyst above $260^\circ C$ it gives diphenylmethane. (25)

With copper catalyst the latter product is obtained above $350^\circ C$ and with active nickel catalyst further reduction to dicyclohexyl methane is observed. Zinc dust distillation yields diphenylmethane accompanied by tetraphenylethane and tetraphenyl ethylene. Sodium plus alcohol yields diphenyl methane although sodium amalgam yields the carbinol. Benzopinacol is formed by aqueous electrolytic reduction and by zinc dust and alcohol (NH_4Cl) but not by calcium, magnesium or aluminum and alcohol. The latter reagents give diphenylcarbinol but magnesium in the presence of bromide or iodide gives the pinacol. Sodium with ammonium chloride in liquid ammonia give diphenylmethane. At 300° ethyl alcohol and sodium alcoholates convert benzophenone to diphenylcarbinol.

Benzophenone is known to form crystalline addition compounds with various halides. Thus, $2(C_6H_5)_2CO \cdot ZrCl_4$; $(C_6H_5)_2CO \cdot TiCl_4$ (orange powder from chloroform); $2(C_6H_5)_2CO \cdot BeCl_2$ (from ether or benzene); $3(C_6H_5)_2CO \cdot MgI_2$ (from ether or benzene); $2(C_6H_5)_2CO \cdot HgCl_2$ (sol. in water, benzene, etc.); $2(C_6H_5)_2CO \cdot 2AlBr_3$; $(C_6H_5)_2CO \cdot AlCl_3$; $(C_6H_5)_2CO \cdot 2SbCl_5$; $(C_6H_5)_2CO \cdot FeCl_3$; $(C_6H_5)_2CO \cdot ZnCl_2$ (yellow-brown oil) $4(C_6H_5)_2CO \cdot ThCl_4$; $2(C_6H_5)_2CO \cdot SnCl_4$; $(C_6H_5)_2CO \cdot SbCl_3$. For the most part these are eutectic compounds and little is known of their properties.*

On warming with PCl_5 , benzophenone gives diphenyldichloromethane. Aqueous acids and alkalis are generally without action on benzophenone under ordinary conditions.

Sodamide reacts with benzophenone yielding a ketyl-like addition product from which the ketone is regenerated by action of water.

* We have found that benzophenone in chloroform or carbontetrachloride solution appears to react with UBr_3 forming a brown slightly soluble product.

3.40. Observations on the Reaction of Sodium Benzophenone Ketyl With UBr_3 .

Sodium benzophenone ketyl was prepared in several media. Initial studies employed diphenyl ether as the medium. The entire reaction and all transfers were carried out anaerobically. Sodium sand was first prepared in sodium-dried diphenyl ether by stirring under argon at 12,000 rpm in a Morton flask. To the fine warm suspension was added an amount of benzophenone sufficient to form the disodium ketyl (four times the weight of the sodium). A deep purple color developed instantly (the rate largely depending on the fineness of the sodium) and the liquid thickened. An equivalent amount of finely powdered UBr_3 (containing a small amount of UBr_4) was added in portions. Each portion changed the purple color to olive drab immediately but in a few seconds the color was restored as more ketyl formed. The reaction was very slightly exothermic but this was difficult to judge. The mixture was left stirring gently overnight at 70-80° when it slowly turned bright red owing to formation of the disodium ketyl. Addition of a small piece of sodium did not change the color but addition of benzophenone caused the mixture to become deep purple. The mixture was stirred for 24 hours at 70°C. and the color was observed to become more drab. The mixture was forced by argon into a sintered glass filter reinforced by Whatman No. 42 paper. A small amount of black slime was retained but the bulk of the suspended matter passed through the filter even on several re-filtrations. Isopropyl alcohol was added to the reaction flask and transferred to the filter. Very little gas evolution was noted indicating no free sodium or ketyl. The combined filtrate and alcohol wash were re-filtered through the black slimy filter disc. The liquid appeared to have blue and grayish suspended matter which could not be removed by filtration but deposited a heavy black precipitate which appeared metallic under the microscope.

The black precipitate was washed by centrifugation with benzene and isopropyl alcohol. Brief exposure to air was unfortunately necessary at this point. The washes showed a strong blue fluorescence comparable to aesculein and a brownish color by transmitted light. A final benzene wash yielded a heavy black precipitate, a faint yellow solution and a light flocculent precipitate on the upper surface. The black material which appeared metallic under the microscope was further washed with isopropyl alcohol, then with ethereal methanol when it became brownish. After brief investigation it was bottled and placed on file.

The original black solid from the reaction was thought to be nearly colloiddally fine uranium and was observed to react with dilute HCl giving bubbles of gas. It gave a strong test for uranium (ferrocyanide) but contained only traces of bromine. A sample submitted for x-ray examination turned yellow before it could be examined. The yellow material gave no diffraction pattern. The black product was observed to be insoluble in organic solvents but peptized in water forming a brownish sol coagulated by sodium hydroxide to a brownish flocculent material. The black material was degassed in high vacuum at ca 200°C. when a small amount of colorless organic liquid distilled out. The black metallic residue had a density of 6.0 and glowed when heated in air. These qualitative observations are in keeping with the assumption that the heavy black material is extremely finely divided uranium. The remainder of the product rapidly discolored and was set aside in the sample reference collection.

A repetition of this run with less solvent (diphenyl ether) and a greater excess of sodium (5.19 g UBr_3 , 2 g. Na, 10 g. $(\text{C}_6\text{H}_5)_2\text{CO}$) was allowed to stand 48 hours at 40°C . The original reaction as the UBr_3 was added was again observed to be mildly exothermic. The color changes occurred as before but the mass became too pasty to handle. The product was diluted with pyridine and slowly turned green. The yellow and black solid resulting gave a strong qualitative test for U and a weak test for Br but did not bubble when added to dil. HCl. The reaction of the addition compound formed by pyridine and sodium with UBr_3 was examined briefly. Pyridine reacts readily with sodium at room temperature forming a labile deep brown flocculent solid. This addition compound gave no evidence of reaction with UBr_3 at room temperature over a period of three months.

A third run using xylene and diphenyl ether as solvents was carried out under hydrogen and allowed to proceed for seven days at 70°C . maximum temperature. There was no evidence of hydrogen absorption during the preparation of the sodium sand nor the initial six hours of the reaction. The brown-black suspension was filtered anaerobically through a fine sinter with great difficulty. A reddish-brown product was formed (probably corresponding to the red disodium ketyl) which on washing with xylene and drying in argon and in vacuo gave a black solid with a white crust. This solid contained residual organic matter, sodium bromide (x-ray), and uranium tribromide (x-ray, faint). Microscopic examination of this particular product gave no evidence of metallic particles.

3.50 Conclusions from Ketyl Studies

The evidence for the formation of metallic uranium by reduction of the tribromide with sodium ketyl is by no means conclusive. In only two runs was a metallic-appearing heavy black product obtained. The evidence that uranium is produced lies in the following observations: a) the presence of UO_2 in the product, which, in view of the established reactivity of finely divided metal and the absence of reactive or hydroxyl oxygen in the reaction mixture (in one case) is most easily explained as arising from the partial oxidation by air of colloidal metal. b) The combustibility of the product when heated in air (the presence of surface oxide and organic matter would prevent pyrophoricity.) c) The evolution of gas with dilute HCl but not water. d) The presence of NaBr in the reaction product. e) The substantial absence of Br^- in the black product.

The failure to obtain an x-ray pattern of uranium and the failure to obtain a density of reasonable magnitude are contrary to the assumption that uranium is formed but might be explained by the colloidal character and the presence of adsorbed organic matter. In all cases the yield of crude product was 5 or 6% more than theoretical for pure uranium. This is not surprising since organic matter and oxygen were present in the product. The apparent reluctance of the ketyl - UBr_3 mixture to take up hydrogen is surprising whether or not colloidal U is present. Presumably at higher temperatures and pressures hydrogen would be taken up.

It seems definite that a slow reaction takes place above 70°C between sodium benzophenone ketyl and UBr_3 and that some NaBr is formed thereby.

Whether or not uranium is formed, the complexity of the reaction, and the difficulty of handling and separating the products would render the reaction of little preparative interest. A painstaking quantitative study of the reaction might be very rewarding however since the mechanism might well involve compounds with a U-C bond.

3.60 The Reduction of UBr_4 by Sodium Sand in Biphenyl (R. Barry)

A considerable number of organic liquids were tested for inertness towards molten sodium at temperatures above $200^\circ C$. Biphenyl appeared to be stable at $250^\circ C$ even in the presence of hydrogen, and all work was based on this medium. (Samples of Monsanto HB-40 were not received in time to be examined. This material is partially hydrogenated terphenyl.)

It was found that UBr_4 reacted quietly and at least in part with sodium sand dispersed in biphenyl under purified argon at $250-265^\circ C$. On cooling, the excess sodium floats to the surface, the presumed uranium and NaBr sink, leaving a stratum of clear biphenyl between. The biphenyl was removed either by leaching with pentane rather than by filtration of the melt. The black solid mixed with NaBr was found to be extremely reactive, and no method of separation was found which did not yield UO_2 or at least partially oxidized product. (The black solid in one instance was observed to react with ordinary diethyl ether.) The presence of NaBr was established by its x-ray diffraction pattern. Large amounts were evidently present.

Accordingly, work on this reaction was postponed pending investigation of means for the separation of NaBr from extremely reactive and finely divided uranium.

* (or by evaporation)

4.00 WORK ON SODIUM NAPHTHALENE DISSOLVED IN ETHYLENE GLYCOL DIMETHYL ETHER. (E.B.D.)

4.10 Introduction

This sodium naphthalene-glycol ether solution is a typical member of a group of reagents which appeared especially promising for bringing sodium into reaction with uranium halides. Here the sodium is bound to naphthalene loosely and reversibly so that in many reactions the solution behaves like a solution of the metal in an inert solvent. At the end of such a reaction, a solution of naphthalene in glycol ether may be filtered from the solid products; this solution is capable of taking up more sodium, and presumably can be recycled repeatedly.

The preparation and properties of solutions of sodium naphthalene in dimethyl ether or in glycol dimethyl ether are described in a paper by Scott, Walker and Hansley (26). The use of a number of other effective solvents, and the formation of addition products of sodium with other aromatic hydrocarbons are disclosed in a series of patents issued to one or more members of this same research team.

Scott, Walker and Hansley have shown that by the use of certain special solvents (such as these methyl ethers) such aromatic hydrocarbons as naphthalene can easily be converted into sodium addition compounds. More than a difference of rate of reaction is involved, since if diethyl ether is added to a solution of sodium naphthalene in dimethyl ether, the compound already formed decomposes into elemental sodium and the original hydrocarbon. The sodium compound of naphthalene is provisionally represented as $C_{10}H_8 \cdot Na_2 \cdot C_{10}H_8$. The presence of the solvent, however, is required for the existence of this sodium compound; evaporation of a solution (in dimethyl ether) gives a dark green solid which changes to gray when the last traces of dimethyl ether are lost; extraction of the gray solid with heptane then leaves a residue of nearly pure sodium.

Similar addition products may be formed with lithium or potassium instead of sodium (28). Instead of pure dimethyl ether, a mixture of the ether with xylene may be used (27). Other effective solvents include such ethers as methyl-ethyl ether, methyl-propyl ether, methyl-isopropyl ether, methylal, glycol formal, dioxane, glycerol trimethyl ether, methyl glycerol formal, and dimethylene pentaerythritol (29, 36), also certain methyl amines (31), and alkylamine aliphatic monoethers (30). Other hydrocarbons which may be used in place of naphthalene include (29) biphenyl, phenanthrene, anthracene, (30) acenaphthene, dinaphthyl, retene, and their homologs.

4.20 Properties and Reactions of Sodium Naphthalene Reagent

The solutions of sodium naphthalene are dark green and have good electrical conductivity.

In reactions with such substances as mercury, oxygen, and benzyl chloride, the sodium naphthalene solution acts simply like a solution of sodium metal (26). The reaction with mercuric or lead salts may be used for preparing mercury-sodium or lead-sodium alloys (35). With water, alcohols, and organic compounds capable of forming sodium derivatives, where sodium replaces hydrogen,

the products are naphthalene, dihydronaphthalene, and the sodium compound of the reactant (26). With carbon dioxide, one mole of naphthalene and one mole of the sodium salt of dihydronaphthalene dicarboxylic acid are formed (27). Gradual hydrolysis or carboxylation in the presence of sodium causes the remaining naphthalene to react with sodium.

4.21 Reaction with UBr_3 and UF_4

Following the directions of Scott, Walker and Hansley, we have prepared seven different batches of sodium naphthalene in glycol dimethyl ether, and have treated portions of these solutions with approximately equivalent samples of uranium tribromide (six experiments) or uranium tetrafluoride (one experiment). In the course of this work, we have gradually developed an apparatus and technic for carrying out the reaction under dry argon, in the absence of oxygen and water. In the latest experiments, we were apparently successful in excluding air during a series of manipulations which continued over several days.

4.211 When dry uranium bromide was treated with sodium naphthalene solution, a vigorous reaction took place on contact, with marked evolution of heat; uranium bromide was blown about in the reaction tube. In one run, the mixture became warm enough to vaporize some of the glycol ether, which condensed in the upper part of the vessel. In the later runs, the initial reaction rate was moderated by moistening the uranium bromide with a little glycol ether before adding sodium naphthalene reagent.

In a typical experiment, 4.0 g. of uranium bromide (containing 26 milliequivalents of bromine) was moistened with 5 ml. of glycol dimethyl ether, then treated with 30 ml. of sodium naphthalene reagent (containing 30 milliequivalents of sodium), added in portions. The uranium bromide, sample "tribromide C - MCC - 11/13/53", a dark brown powder, was presumably a mixture of UBr_3 and UBr_4 ; according to analyses by M.C.C. it contained 45.9% uranium and 52.2% bromine. The following description is based on this experiment, but it includes details observed in other similar runs.

4.212 When the uranium bromide was stirred with redistilled, anhydrous, air-free glycol dimethyl ether, the mixture became definitely warm; a deep purple slurry was formed, which on standing separated into a purple precipitate and a green solution. When 5 ml. of sodium naphthalene reagent was added, further warming occurred; the purple precipitate turned brown, while the supernatant solution became wine-red. With additional 5-ml. portions of sodium naphthalene reagent, the precipitate grew progressively darker, while the solution remained red. After a total of 26 ml. of sodium naphthalene reagent (presumably equivalent to the bromine present), the precipitate was black, the solution, pink. With the addition of 4 ml. more of the reagent, the supernatant solution took on the dark green color of the excess sodium naphthalene, and this color persisted on standing over night. At this time, the black precipitate contained, in addition to dense particles which settled rapidly, a quantity of less dense, finely divided material which remained in suspension for a long time. This lighter solid apparently contained a substance which dissolved in glycol ether to give a red solution.

After the black precipitate had settled on standing over night, the dark green supernatant solution was decanted. The precipitate was washed repeatedly by decantation with glycol dimethyl ether until the washings, deep red at first, became only faintly colored. The dense black precipitate was then transferred with glycol ether to a sintered glass filter and filtered with suction. In transferring the last few black particles, it could be observed that some of them were reacting with the glycol ether (or with something contained in it) to form a light gray solid. (This occurred in spite of precautions to keep the ether anhydrous and free from dissolved air.) The filter-cake was then washed with several portions of petroleum ether (dried over sodium), then with several portions of diethyl ether (distilled from sodium), and was dried in an atmosphere of argon. The product, a gray powder, was removed from the filter tube in the drybox, weighed, and bottled in an atmosphere of dry nitrogen. Its weight, 5.25 g., was 0.65 g. greater than the original weight of uranium bromide plus the weight of sodium equivalent to the bromine, indicating that this sample contained more than uranium, bromine, and sodium.

4.213 Several attempts have been made to get an X-ray diffraction pattern which would identify the constituents of this mixture. The patterns which were obtained, however, gave no indication of the presence of free or combined uranium, showing only lines characteristic of sodium bromide. We must conclude that the particles of product containing uranium were either too coarse to enter the capillaries used for holding the sample in the X-ray camera, or that they were not properly crystallized for the production of an X-ray pattern.

In one trial, a sample of powder was transferred in the drybox to a Pyrex glass manifold, in which it was kept all night under vacuum to remove volatile material. The manifold was then filled with argon and subjected to intense vibration to pulverize the sample, and to cause a portion of the powder to flow into an attached capillary tube in which it was sealed for X-ray examination. After this treatment, the powder remaining in the manifold, on exposure to air, was found to contain numerous particles of pyrophoric material.

4.214 Further information about this reaction has been gained from examination of the mother liquor filtered from the solid reaction products. The colors of the solution observed during the reaction, however, tell us little or nothing about the state of the uranium present in the mixture, since similar colors are produced when sodium naphthalene is oxidized in the absence of uranium. In an experiment in which a slow stream of dry air was bubbled through a sample of sodium naphthalene reagent, the dark green solution gradually turned red, with a red solid separating out; on further treatment, the red mixture changed to a yellow solution, with a yellow-brown gelatinous precipitate. A finely divided black precipitate is commonly found in sodium naphthalene reagent which has been allowed to stand for a few days.

4.215 Chemical tests on the mother liquor filtered from the solid reaction products indicate that the sodium naphthalene reagent has reacted directly with the $U\text{Br}_3$, rather than with HBr formed by solvolysis. Direct reduction of $U\text{Br}_3$ by the reagent should leave the naphthalene unchanged in the mother liquor, while reaction with HBr should convert half the naphthalene to dihydronaphthalene. It is found that the filtrate from the solid reaction products does not decolorize

Br_2 or KMnO_4 , hence appears to contain no dihydronaphthalene. For comparison, a sample of sodium naphthalene reagent was decolorized by treatment with (aqueous) HCl dissolved in glycol ether; the resulting neutral solution decolorized several milliliters of KMnO_4 solution.

The filtrate does contain naphthalene, which will combine with more sodium to form the dark green addition compound. A rough estimate of the amount of sodium naphthalene which had been formed was obtained from the volume of isopropyl alcohol (diluted with glycol ether) required to discharge the green color; it appeared that more than half of the original naphthalene had been recovered.

4.216 In two other runs with uranium bromide, similar to the one just described, attempts were made to use alcohols for extracting the washed filter-cake of mixed solid reaction products. In the first of these experiments, the filter-cake was treated with 5 ml. of absolute methanol. A vigorous reaction occurred at once, with warming and much bubbling, apparently from evolution of gas. When the reaction was over, any excess methanol had evidently been absorbed by the filter-cake, since little or no liquid could be removed by suction filtration. Extraction of the mixture with isopropyl alcohol then yielded a dark brown filtrate, which contained much uranium.

Similar behavior was observed when a second filter-cake was extracted with (nearly) anhydrous isopropyl alcohol. (Experiments in this laboratory had suggested that aqueous isopropyl alcohol might prove suitable for extracting sodium bromide from the mixture.) This mixture, however, reacted vigorously with the anhydrous alcohol, with perceptible warming, evolution of a considerable volume of gas, and formation of a deep brown solution. When this solution was exposed to air, an olive-green precipitate separated, leaving a colorless supernatant liquor. Under anaerobic conditions, however, the deep brown solution proved stable, showing no change after three weeks. Evaporating the solution to dryness left a brown, glassy residue, which was somewhat soluble in petroleum ether, and redissolved readily in isopropyl alcohol. The solid residue contained much uranium, but no significant amount of bromine.

4.217 In still another experiment with uranium bromide, in which a large excess of sodium naphthalene reagent was used, a true or colloidal solution in glycol ether was formed, which contained a large proportion of the uranium. The initial reaction had yielded the usual dense black precipitate, with a colorless supernatant solution. (The previously described red color of the supernatant liquor is easily lost if strictly anaerobic conditions are not maintained.) The clear solution was decanted and replaced by 12 ml. of sodium naphthalene solution (a large excess, about 40% of the calculated amount), and this mixture was allowed to stand for two days before filtration. The slurry then proved difficult to filter, containing finely divided precipitate which clogged the sintered glass disc. In transferring the precipitate to the filter, a sample of glycol ether was used which had been dried by the addition of enough sodium naphthalene solution to give a permanent light green color. This procedure proved ill-advised; on standing, the pale green solution decomposed with formation of a bulky black precipitate. When the filter-cake was washed with a pure, dry sample of glycol ether, a dark brown, nearly black filtrate was obtained. This was evidently

either a true solution or a stable colloid, since a portion showed no sign of settling after standing for five days. On exposure to air, a dark olive-green to black precipitate separated from this filtrate, leaving a pale, yellow-brown supernatant liquid. This liquid contained only a trace of non-volatile inorganic material, no uranium; the precipitate contained much uranium, only a trace of bromide, and no non-volatile organic compound.

The uranium present in this solution may have been in the form of (7.) colloidal metal, or (8.) methoxide, formed by cleavage of the ether. It may be significant that dark brown solutions of similar appearance were obtained when the solid reaction products were extracted with methyl or isopropyl alcohol.

4.218 In the one experiment with uranium tetrafluoride, 2.0 g. of a commercial sample of UF_4 was treated with 25 ml. of sodium naphthalene solution, containing one equivalent of sodium per liter. After the mixture had been stirred (under argon) for one hour, with no apparent change, the reaction tube was stoppered tightly and allowed to stand at room temperature with occasional shaking. A very gradual change occurred, until, after three months, the green colors of UF_4 and sodium naphthalene had disappeared, leaving a black precipitate covered with a pale greenish-yellow solution. The mixture was then transferred, under argon, to the anaerobic filtration apparatus used in the experiments with uranium bromide, and was filtered with suction. The brownish yellow mother liquor contained only organic material. The black filter-cake was extracted three times with dry petroleum ether, then three times with ethyl ether (distilled from sodium). The filter-cake then appeared black when wet, dark gray, coated with white, when dry. After drying in argon, the cake was removed under nitrogen in the drybox. A small amount of product remaining on the filter was then extracted with water: the extract gave no test for uranium, but gave a large, white precipitate, presumably CaF_2 , with calcium acetate. A small black residue remaining on the filter dissolved readily in cold, concentrated hydrochloric acid.

4.30 Details of Preparation of Sodium Naphthalene Reagent

Our preparations of sodium naphthalene solution have been carried out in 250-ml. batches. The reaction vessel was a 500-ml. 3-necked Pyrex flask, provided with a Hershberg stirrer, the shaft of which entered the center neck of the flask through a gas-tight bearing (Ace 8239 stirrer seal). One side neck of the flask was fitted with a rubber stopper carrying a thermometer and an inlet tube for argon; the third neck carried the exit tube for argon, which escaped through a small trap sealed with dibutyl phthalate. The argon, from a steel cylinder, was passed through a tower filled with Drierite; in the later runs, it was also passed through a tower or wash bottle containing a reagent for removing oxygen.

4.301 Attempts were made to use the sodium naphthalene reagent itself for removing oxygen from argon; it was evidently effective for a time, but the absorption bottle soon became clogged with a copious black precipitate. In one run, the argon was bubbled through a Drechsel gas-washing bottle containing liquid sodium-potassium alloy. More recently, we have used a tower packed with

Drierite granules coated with sodium-potassium alloy; the liquid metal wets the Drierite readily, and adheres to it firmly, providing a bright, metallic surface. The tower is filled under nitrogen in the drybox. This appears to be a particularly safe and efficient method for using sodium-potassium alloy in purifying gases.

4.302 In the reaction flask was placed 32 g. (0.25 mole) of naphthalene (E.K.Co. no. 168), with enough glycol dimethyl ether to make 250 ml. of solution. In the first run, the ether (Ansul Chemical Co. no. 121) from a freshly opened tin was used as received; in all later runs the ether was dried over sodium ribbon, then distilled in an all-glass still which delivered the distillate directly into the reaction vessel. In the most recent runs the distillation was carried out in a current of purified argon. After the reaction flask had been thoroughly flushed out with argon, 6.25 to 6.5 g. of sodium was added in the form of small blocks, freshly cut under oil, and rinsed with petroleum ether or hexane. Most of the film of volatile solvent coating the sodium evaporated in the stream of argon as the sodium passed through the neck of the reaction flask. With a slow stream of argon flowing through the reaction vessel, the mixture was stirred gently for two hours or more. The solution began to turn green almost immediately, and became opaque within less than five minutes. The reaction is only slightly exothermic; by cooling the flask from time to time in a cold kerosene-bath, the temperature was kept between 20 and 25°C. After two hours at this temperature the reaction was assumed to be complete.

Samples of the reagent for use in experiments were removed by hypodermic syringe. In the later runs, the neck of the reaction flask was closed with a gum rubber cap, through which the hypodermic needle could be inserted without opening the flask.

The sodium naphthalene reagent, standing under dry argon, remained active for at least several days. A finely divided black precipitate formed gradually; this decomposition was apparently accelerated by exposure to air, and possibly would not occur under strictly anaerobic conditions. When the reagent was decomposed with alcohol or water, the black precipitate also was converted into white or colorless material.

4.40 Apparatus

The anaerobic filtration apparatus used in the experiments with uranium halides is shown schematically in Figure 4.1. The actual apparatus was somewhat more compact than the arrangement shown in the diagram, not all parts lying in the same plane; this permitted placing the apparatus in our vacuum oven for drying.

In use, tube A is closed by a gum rubber cap (Davol 150) through which liquids can be introduced from a hypodermic syringe. Also, when the apparatus is flushed out with a stream of argon, it is convenient to let the gas escape through a hypodermic needle inserted through the rubber cap. The stopcock below the cap serves as further protection against leakage of air through the cap in prolonged experiments.

The reaction with uranium halide was carried out in tube B. The sample of uranium salt was weighed and placed in tube B in an atmosphere of dry nitrogen in the drybox, and the apparatus was tightly stoppered. The nitrogen in the apparatus was replaced by argon before the sodium reagent was added. At the start, the mouth of tube B is closed by a rubber stopper through which passes a stainless steel stirrer with a nearly gas-tight bronze bearing (Fisher 14-512). A rubber sleeve covering the stirrer shaft and the end of the bearing makes this joint vacuum-tight at times when the apparatus does not contain argon at more than atmospheric pressure. When the stirrer is no longer needed, this stopper is removed under protection of a vigorous stream of argon, and replaced by a solid rubber stopper.

By tilting the apparatus, liquid or slurry in B can be poured through the connecting tube on to the sintered glass disc in chamber C. The mouth of C is closed by a rubber stopper carrying a tube, with stopcock, through which argon is admitted to the apparatus. The rate of filtration is controlled by stopcock E. The filtrate is received in tube D. A stopper in the mouth of this tube carries a tube, with stopcock, leading through a drying tower to a vacuum pump.

Tubes B and D are connected by a tube with stopcock F, through which volatile solvents in D can be distilled back into B for recirculation. In this operation, the liquid in D is first chilled in a dry-ice-acetone bath while the apparatus is evacuated. Tube B is then cooled in the freezing-bath, while the liquid in D is boiled under reduced pressure. In this way, a small quantity of volatile solvent can be recycled repeatedly in a closed system. Inert solvents, such as ether, can be dried by adding a small piece of sodium ribbon to the liquid in bulb D.

4.50 Discussion of Results of Reduction Reactions.

It has been established that uranium tribromide and tetrafluoride react with the sodium naphthalene-glycol dimethyl ether reagent. It has not yet been demonstrated that uranium metal is produced in this reaction, although our observations may be considered consistent with this interpretation. The reaction products have been found to contain pyrophoric material.

In the case of the bromide, at least, the vigorous initial reaction can hardly be explained except as involving reduction of the uranium salt. We do not know, however, whether the product is uranium metal or some uranium compound of intermediate valence. With both UBr_3 and UF_4 , the halogen was removed from the uranium with the formation of sodium halide. The black precipitate evidently contained sodium halide, uranium in some form (metal, oxide, or organic derivative), and possibly some insoluble decomposition product of sodium naphthalene (which may still contain reactive sodium). The unexpectedly great reactivity of the uranium (or uranium compound) which is formed has prevented the isolation of this material from the other solid reaction products for identification and analysis.

The brown solution formed when the solid reaction products were extracted with isopropyl alcohol presumably contained a uranium isopropoxide. To obtain further information about uranium isopropoxides and related compounds, we have studied the reactions which occur when uranium bromide is dissolved in iso-

propyl alcohol, and when this solution is treated with sodium isopropoxide, or with metallic sodium. This last experiment was designed to simulate conditions in certain experiments where isopropyl alcohol was used to extract reaction mixtures containing unreacted uranium bromide and metallic sodium.

5.00 WORK ON POSSIBLE LEACHING REAGENTS

5.10 Reaction of Uranium Bromide with Isopropyl Alcohol.(E.B.D.)

The reaction of uranium bromide with isopropyl alcohol has been studied at room temperature under anaerobic conditions. It is found that the bromide undergoes partial solvolysis, one atom of Br being replaced by OC_3H_7 .

The uranium bromide, sample "tribromide C, MCC, 11/13/53", a dark brown powder, may have contained nearly 30% of tetrabromide, according to analyses by M.C.C. showing 45.9% uranium and 52.2% bromine; its average composition may be represented by the formula $\text{UBr}_{3.39}$. Reagent grade isopropyl alcohol was dried over Drierite and distilled, either in vacuo or in a current of dry nitrogen or argon.

The uranium bromide, treated with isopropyl alcohol, gave first a red solid in a brilliant red solution; after a few seconds, a pale green precipitate began to form; within two or three minutes all had been converted to light green solid covered by a deeper, emerald green solution. This solution was acid (pH about 2 by Hydrion paper) and contained both uranium and bromide. The reaction was accompanied by perceptible warming, and apparently by evolution of gas. An attempt to measure this gas, however, showed no greater increase in volume than might be expected from the evaporation of enough alcohol to saturate the argon present in the vessel. The precipitate, filtered off and dried in vacuo at room temperature, was a dark olive-green solid (sample C). The filtrate, evaporated nearly to dryness, left a lighter green, sticky paste. On further drying in vacuo this paste was converted to a light olive-drab powder (sample D). This powder redissolved slowly, but apparently completely, in isopropyl alcohol.

Analyses of these two solid products, reporting the percentages of carbon, hydrogen, and ash, are given in the following table. In interpreting these data, it is assumed that the ash consisted of U_3O_8 . The analytical data are consistent with the assumption that one bromine atom of the tribromide, and one bromine atom of the tetrabromide were replaced by OC_3H_7 , yielding a mixture of $\text{UBr}_2\text{OC}_3\text{H}_7$ and $\text{UBr}_3\text{OC}_3\text{H}_7$. The average composition of the product is assumed to be $\text{UBr}_{2.39}\text{OC}_3\text{H}_7$ (based on $\text{UBr}_{3.39}$ as the formula of the starting material). In the table we have included for comparison data calculated for the solvolyzed tribromide and tetrabromide, and also for the mixed product represented by the above formula.

<u>Substance</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Ash (U_3O_8)</u>
Sample C (less soluble)	8.2%	1.7%	57.4%)*
Sample D (more soluble)	6.1%	1.5%	58.3%)*
$\text{UBr}_{2.39}\text{OC}_3\text{H}_7$	7.4%	1.4%	57.5%)**
$\text{UBr}_2\text{OC}_3\text{H}_7$	7.9%	1.5%	61.4%)**
$\text{UBr}_3\text{OC}_3\text{H}_7$	6.7%	1.3%	52.3%)**

*Observed **Calculated

On the basis of the percentage of carbon found, it appears that the more soluble portion of the product contained more of the uranium IV compound.

This assumed composition of the product is also consistent with the weight of product formed in the run in which these two samples were prepared. Starting with 2.00 g. of $\text{UBr}_{3.39}$, 0.77 g. of sample C and 0.98 g. of sample D were obtained. After these samples had been removed, the solid product remaining in the apparatus was dissolved in dilute nitric acid, and the bromine content of the solution was determined by precipitation of silver bromide: recovered, 0.17 g. of AgBr . After correcting for lost product equivalent to 0.17 g. of AgBr , the observed and calculated values for the weight of product are found to be in excellent agreement.

1.92 g.	$\text{UBr}_{2.39}\text{OC}_3\text{H}_7$	equivalent to 2.00 g. $\text{UBr}_{3.39}$
<u>-.18 g.</u>	"	" " 0.17 g. AgBr
1.74 g.	"	net product (calculated)

0.77 g. sample C

0.98 g. sample D

1.75 g. total product recovered.

Some of the products obtained from this reaction have proved to be unexpectedly soluble in petroleum ether, but their behavior has not been consistent. Since their solubility seems to be decreased by drying, it may depend on the presence of isopropyl alcohol.

5.20 Reaction of Uranium Bromide with Sodium Isopropoxide

Investigation of the reaction between uranium bromide and sodium isopropoxide has proved more difficult because several different products are formed, and because these products are extremely sensitive to air.

When the green slurry formed by uranium bromide in isopropyl alcohol was treated with an equivalent amount of sodium isopropoxide solution, the green precipitate dissolved, while a grayish precipitate of sodium bromide separated slowly. In earlier experiments, a dark brown solution was formed; in later runs, with improved anaerobic technic, the solution was green. In these later runs, the sodium isopropoxide solution was prepared by dissolving a freshly trimmed block of sodium, under an atmosphere of nitrogen, in a sample of isopropyl alcohol which had been dried over Drierite and distilled in a current of dry nitrogen. The solution was stored under nitrogen in a flask closed with a gum-rubber cap. Samples of the solution were removed by inserting the needle of a hypodermic syringe through this cap.

In one such experiment (using the anaerobic filter described in an earlier section), 1.00 g. of uranium bromide in 5 ml. of isopropyl alcohol was

treated with 40 ml. of 0.163 molar isopropoxide solution. After standing overnight, the solution was filtered with suction; the filtrate was a clear dark green, nearly black solution, yellow-green by transmitted light. The filtrate was evaporated in vacuo at room temperature. When the volume had been reduced to about 5 ml., the solution was still dark green, and a dark green solid had separated. Soon afterward it was observed that the solid and the solution had turned dark brown, apparently as a result of leakage of air through stopcocks in which the lubricant had not remained vacuum-tight. After evaporation to dryness, during which further leakage occurred, 0.52 g. of dark brown powder was recovered. A grayish-white filter-cake of sodium bromide weighed 0.51 g.

Analysis of this brown powder showed 10.4% C, 2.1% H, and 68.1% ash. Assuming that the ash consisted of U_3O_8 , these data indicate that the product contained only about one OC_3H_7 group per atom of U. Since at least 75% of the bromine present was recovered as NaBr, it is evident that oxidation of the product had been severe.

In another experiment, a slurry made from 2.00 g. of uranium bromide in 10 ml. of anhydrous, air-free isopropyl alcohol was treated with small pellets of metallic sodium weighing 0.35 g., all told. After about two and one half hours, when nearly all the sodium had reacted, 25 ml. more isopropyl alcohol was added. The reaction appeared complete after three hours. After standing over night, a small, dense, dark brown precipitate, and a bulky gray precipitate (of sodium bromide) had settled, leaving a clear green solution. This solution, filtered with suction and evaporated in vacuo at room temperature, left a mixture of green and white, apparently crystalline solids (sample I). The mixed brown and gray precipitates (filtered from the solution of sample I) contained nothing which could be extracted with petroleum ether. By extracting them with anhydrous methanol and evaporating the extract to dryness, 1.00 g. of somewhat dirty white crystals of sodium bromide were recovered. Left behind on the filter was 0.28 g. of black powder, apparently formed by the action of methanol on the brown precipitate.

The mixture of green and white solids (sample I) removed from the apparatus weighed 1.41 g. Tests on a small amount of this same material left behind in the apparatus showed that it contained a fraction which dissolved in petroleum ether to yield a brown solution. A white residue, insoluble in petroleum ether, was still soluble in isopropyl alcohol; it contained much uranium, only a small amount of bromide.

Extractions with petroleum ether and with isopropyl alcohol were then repeated on the 1.41 g. main portion of sample I. Treatment with four 15-ml. portions of petroleum ether apparently removed all of the soluble constituent. When the dark brown extract was concentrated to 15 ml. by evaporation in vacuo, a large amount of buff-colored solid separated, which did not redissolve in petroleum ether. After filtering off this precipitate (sample C), the remaining clear brown solution was evaporated in vacuo at room temperature to a dark brown, very viscous liquid, perhaps containing some solid material. When pumping for many hours at room temperature failed to remove all the liquid from this sample, it was pumped (with Pressovac pump)

for 3 hours at 100°C. This treatment drove off a few drops of a high-boiling, water-white liquid, leaving a crust of khaki-colored solid, sample B.

Three determinations of C and H on sample B have been carried out in this laboratory by E.J.G. and M.C.C.; one determination of C, H, and ash has been made (on a very small sample) in another laboratory. The results, tabulated below, indicate that this khaki-colored solid may be identified as $U(OC_3H_7)_3$.

	Carbon	Hydrogen	Ash (U_3O_8)
Calculated for $U(OC_3H_7)_3$	26.02%	5.10%	67.6%
Observed (1)	26.30%	4.71%	-----
(2)	26.31%	4.98%	-----
(3)	23.76%	4.38%	-----
(4)	21.0 %	3.9 %	68.3%

The buff-colored precipitate (sample C) which separated from the petroleum ether solution proved to be still soluble in isopropyl alcohol, forming a cloudy, olive-brown solution. On attempting to filter this solution, nearly all was decomposed as a result of leakage of air. Tests on a very small amount of undamaged product showed that it contained a large proportion of uranium, not more than a trace of bromine.

The solid residue left after extraction of sample I with petroleum ether was no longer white, but tan-colored. Only a small portion of this solid now dissolved in isopropyl alcohol, although the entire sample had formerly been soluble. After evaporating the alcohol solution to dryness in vacuo at room temperature, a light yellow-gray film was left, from which a few milligrams of gummy solid could be scraped. After this gummy material had been dried in a good vacuum for 29 hours at room temperature, until the lumps were no longer sticky, a 7.7 mg. sample was analyzed for C and H; found, 34.94% C, 5.34% H. While this high percentage of carbon might indicate the presence of $NaU(OC_3H_7)_6$ - calculated: 35.12% C, 6.88% H - it is possible that it merely shows that all of the solvent isopropyl alcohol had not been removed.

The tan-colored residue, which no longer dissolved in isopropyl alcohol had evidently undergone serious oxidation or hydrolysis. Two analyses of this material showed only 5.90 and 6.45% C, 1.36 and 1.61% H.

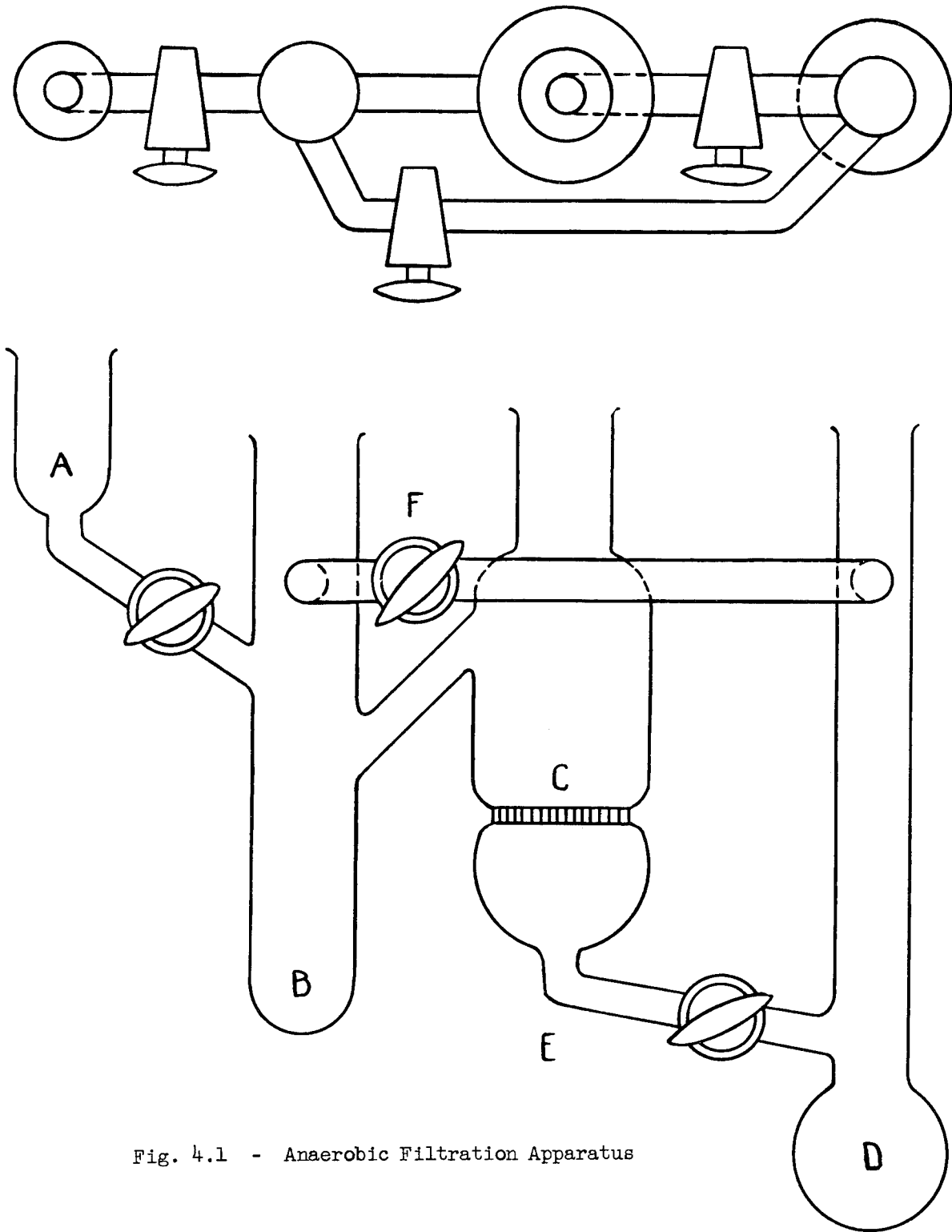


Fig. 4.1 - Anaerobic Filtration Apparatus

5.30 The Reaction of Finely Divided Uranium with Water, Alcohols and Acetone. (R.J. Barry)

Evidence that colloidal uranium reacts with isopropyl and aqueous isopropyl alcohol was referred to earlier.⁽⁴²⁾ This was not foreseen because of statements to the contrary in the literature. A study of the reaction of uranium and other reduction products with possible leaching agents was undertaken. The leaching agents considered were those in which sodium bromide is known to be soluble, viz. water, dilute aqueous sodium hydroxide, commercial isopropyl alcohol, aqueous isopropyl alcohol, methanol and methanol-diethyl ether.

Powdered uranium was prepared by hydriding massive metal at 225°C in a Pyrex tube joined to a manifold and, in the same vessel, pumping off hydrogen at 150-300°C. By using minimum temperature it was found possible largely to avoid sintering of the freshly formed uranium. It was found preferable however to "dehydride" in the presence of a few steel 1/4" ball-bearings agitated by a 60-cycle solenoid vibrator. By this means extremely fine uranium powder could be obtained in a final vacuum of 0.03 microns at 200°C.

Purified argon was admitted to the vessel and the stopcock connecting it to the manifold was opened. The powder was transferred to several ampoules attached by short lengths of rubber pressure tubing to the manifold. The liquids to be tested were degassed, and then injected into the ampoules by means of an hypodermic needle passed through the short rubber tubing connectors. This technique permitted observations to be made on uranium powder whose surface was entirely free of adsorbed air or other impurities. In some cases the ampoules were left attached to the manifold; otherwise they were pinched off and detached.

Water was observed to react rapidly, evolving bubbles of gas (subsequently found to be combustible and presumed to be hydrogen) and forming an olive-drab suspension. Tap water reacted at about the same rate as degassed distilled water. The following table summarizes the observations:

<u>LIQUID</u>	<u>REACTION</u>	<u>APPEARANCE OF PRODUCTS</u>
Water	Rapid evolution of bubbles	Olive drab
Aq. NaOH (pH 8.5)	Similar but slower	" "
Aq. NaOH (ca 1%)	Rapid evolution of bubbles	" green
Isopropyl alc.	v. slt. bubbling	Green crystals formed (24 hrs)
Isopropyl alc. (CaH ₂) dried	No immediate action	-----
Above plus drop of water	v. slt. bubbling	-----
Ether-methanol	Not perceptible	Discoloration, but still metallic
Acetone (dist. from CaSO ₄)	v. slt. bubbling	Unchanged

5.40 The Reaction of Finely Divided Uranium with Gaseous and Liquid Ammonia. (R. Barry)

Uranium prepared by degassing the hydride at slightly higher temperature was screened in a nitrogen-filled drybox and exposed for 20 minutes at -33 to -78°C to anhydrous liquid ammonia. This liquid was obtained by distillation from a solution of sodium in liquid ammonia and was considered to be completely free of moisture. The liquid ammonia was distilled off at -33°C so that the uranium was never in contact with gaseous ammonia above this temperature. Kjeldahl analysis of the residue showed no ammonia present (actually 0.003 meq. less than the blank).

A small bulb of -150 mesh uranium of the above purity was exposed to scrupulously dry ammonia gas at room temperature and pressure in an apparatus connected to a mercury manometer which was used to indicate changes in gas volume. A slight contraction of the gas volume was noted initially followed by a slow expansion overnight. The net small change in volume is probably not significant. The bulb of uranium powder was then placed in boiling water and left for an hour. No significant change in volume was noted at this temperature. It was concluded that interaction of uranium with ammonia at these temperatures was negligible.

5.50 The Reaction of UBr_3 with Liquid Ammonia (R. Barry)

This work was undertaken simply as a qualitative check on the feasibility of leaching reduction mixtures with liquid ammonia. Such mixtures might contain U (or UH_3) UBr_3 , Na, NaBr. The latter two compounds are extremely soluble in liquid ammonia.

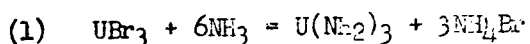
Anhydrous liquid ammonia reacts with UBr_3 (containing some UBr_4) forming a very bulky mixture of solid products, and a greenish solution. The solution contains a large amount of NH_4Br (x-ray pattern, microscopic determination of refractive index) and some uranium compound presumed to be the tetramide or some partially solvolyzed halide. The solid, which effectively plugged all filters tried, was sufficiently bulky to warrant the statement that liquid ammonia is not suitable for the leaching of reduction mixtures.

While this observation was all that was sought for in the tests carried out, the work is being continued briefly in an effort to establish the nature of the products. It seems likely that these include the above-mentioned amides accompanied by several molecules of ammonia of crystallization. No description or properties of uranium amides could be found in the literature except for a cursory description by C.A. Kraus (43) of the UBr_4 product with liquid ammonia.

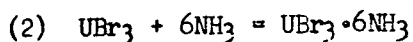
Kraus noted formation of a slightly soluble light green material when UBr_4 was exposed to liquid ammonia. He did not, however, study UBr_3 . Reaction of the latter with liquid ammonia to form green $\text{UBr}_3 \cdot 6\text{NH}_3$ has been reported. (44)

Our studies to date do not agree with the previous reports in that we have what appears to be evidence of the formation of an amide. Thus substantial amounts of NH_4Br are formed by the reaction of UBr_3 (containing UBr_4 and having the composition $\text{UBr}_3 \cdot 46$) with liquid ammonia.

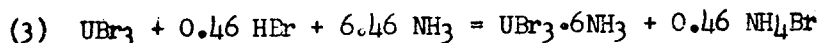
This NH_4Br adequately identified by its x-ray powder pattern and refractive index is present in considerable quantity. While its presence might be explained as a consequence of HBr in the UBr_3 (ie $\text{UBr}_3 \cdot 0.46\text{HBr} \approx \text{UBr}_3 \cdot 46$) it is more reasonable to suppose that it arises from some such reaction as:



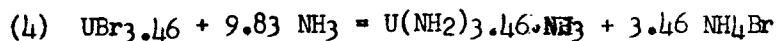
Moreover our $\text{UBr}_3 \cdot 46$ did not evolve hydrogen on reaction with sodium sand which argues for the absence of HBr . If no amide is formed, no NH_4Br will be present as indicated by the reaction:



In the presence of HBr as an impurity in the tribromide, NH_4Br will be formed in accordance with the equation:



A material balance indicates that approximately 10.38 moles of ammonia (actually 10.66) are taken up by one mole of $\text{UBr}_3 \cdot 46$ in accordance with the proposed reaction:



A portion of the ammonia corresponding roughly to 3 moles is eliminated by evacuating the solid product at room temperature and presumably corresponds to the ammonia of crystallization indicated.

This latter equation is supported by failure to detect Br^- in an aqueous suspension of the ammonia-insoluble material assumed to be $\text{U}(\text{NH}_2)_3 \cdot 46$. If the latter were $\text{UBr}_3 \cdot 6\text{NH}_3$ or a partially ammonolyzed material such as $\text{UBr}_2(\text{NH}_2) \cdot n \text{NH}_3$ then Br^- would certainly be present in an aqueous suspension due to hydrolysis. This one negative test for Br^- is by no means conclusive and a similar test made on a different batch was positive. However, it is obvious that any NH_4Br entrained in the ammonia-insoluble product would yield a positive test for Br^- in an aqueous suspension. The negative test is therefore held to be significant.

We therefore suspect that $\text{U}(\text{NH}_2)_3$ and possibly $\text{U}(\text{NH}_2)_4$ may be formed by the action of liquid ammonia on UBr_3 . Judging from the green color of the solution, which is characteristic of U^{IV} it seems likely that the alleged triamide is insoluble in liquid ammonia and the tetraamide sparingly soluble. Additional work is needed to verify the tentative conclusions given and this work is currently in progress. It is interesting that $\text{U}(\text{NH}_2)_3$ if it indeed exists, contains 61% by weight more hydrogen than UH_3 and $\text{U}(\text{NH}_2)_4$ contains slightly more than twice as much hydrogen as UH_3 .

6.00 X-RAY DIFFRACTION ANALYSIS AND DENSITY DETERMINATIONS ON URANIUM HYDRIDE
(E.J.G.)

6.01 Carbon and Hydrogen

A micro combustion train of the Pregl type has been set up for the determination of carbon and hydrogen in organometallic compounds and metal hydrides. Oxygen from a tank passes through a mineral oil bubbler, then to a pressure regulator, and next to a pre-heating unit. The pre-heating unit consists of a small electric furnace and a Vycor combustion tube that is packed with asbestos on each end, with the center being packed loosely with copper oxide wire. The temperature of the pre-heating unit is controlled at approximately 300°C. From the pre-heater the oxygen continues through a sulfuric acid bubble counter to a U-tube that is packed with Ascarite in one arm and magnesium perchlorate in the other. The oxygen flow then continues to a quartz combustion tube, which has a combustion chamber approximately 25.0 mm. I.D. and 300 mm. long. It is closed with a rubber stopper, which is protected from the radiant heat of the Meeker burners by a series of aluminum foil discs used as baffles. The other end of the combustion chamber is reduced to approximately 12 mm. O.D. and is sealed to a tube approximately 350 mm. long. The half-inch tube is reduced at the exit end and is sealed to a piece of 3 mm. O.D. tubing which is 35 mm. long. This combustion tube is packed in the following manner: at the exit end, a ball of silver wool is set in place, followed by a half-inch of asbestos. The tube is then filled loosely with copper oxide wire, followed by another half-inch of asbestos. The packing is terminated by a ball of silver wool. The furnace that holds the combustion tube is held at 700°C. Two standard Friedrich micro absorption tubes are attached by impregnated rubber tubing to the outlet of the combustion tube. The water tube is filled with Anhydrone. The carbon dioxide tube contains Ascarite for two-thirds of the length of the inside tube and Anhydrone in the remaining space. An absorption tube filled with Anhydrone is inserted between the second Friedrich tube and a Mariotte bottle.

Air-sensitive samples are wrapped and weighed in tin-foil. A quartz boat about 10x15x40 mm. is employed for holding the sample in the combustion tube. At first the sample is slowly burned by using a Bunsen burner, followed by a final combustion with two Meeker burners. It is necessary to maintain a constant flow of oxygen through the system during the period of maximum combustion. A blank is determined every day by burning a sample of tin. Percent carbon and hydrogen are calculated from the gain in weight of the Friedrich tubes less the correction for blank.

By careful observations of details and use of a standardized procedure, excellent results may be obtained by such a combination method. We prefer this technique to the vacuum fusion and related procedures. It is probable that the use of tin accelerates the removal and combustion of hydrogen in metallic or saline hydrides.

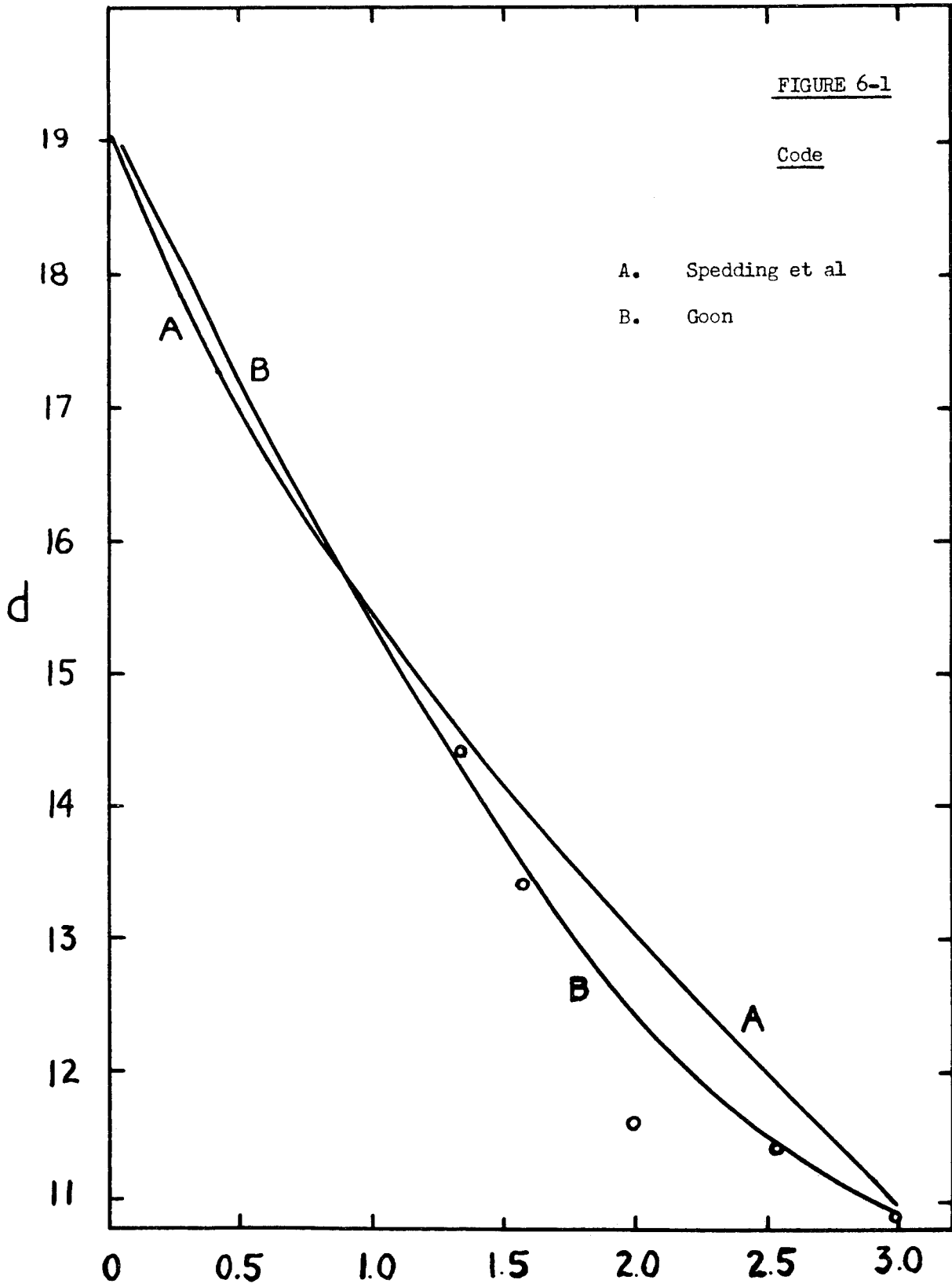
6.02 DENSITY OF URANIUM HYDRIDE - URANIUM MIXTURES

Densities of partially dehydrated UH_3 have been determined by the helium displacement method. Hydrogen analyses were made simultaneously (by combustion). Assuming the samples to contain only uranium and hydrogen, the composition of each sample was calculated. A plot of density versus UH_n , where n is less than three was made. The results are compared with those of Spedding (37) in Figure 6-1. Samples of UH_n were prepared by dehydrating samples of $\text{UH}_{2.8}$ at one micron pressure and at a maximum temperature of 250°C for various lengths of time. X-ray diffraction analysis of the UH_n samples indicated the presence of two phases (uranium and UH_3), only at composition $\text{UH}_{1.33}$. When n is greater than 1.33 X-ray patterns indicated only the presence of UH_3 .

A possible explanation for our finding a greater curvature in our plot than that by Spedding is offered. It is entirely possible that on dehydrating samples of UH_3 , hydrogen atoms are removed from the UH_3 lattice leaving the lattice intact but with a deficiency of hydrogen atoms. Density measurement on such samples would then give an observed value which is closer to the density of UH_3 than would be predicted for a discrete mixture of uranium and hydride. As stated above, X-ray diffraction analysis indicated the presence of both phases U and UH_3 only in sample $\text{UH}_{1.33}$. These results are quite different from the later (1943) results of Spedding, and Nottorf (38) who report a linear relation between d and n and who further note the X-ray patterns of both U and UH_3 in specimens of UH_n over a wide range of compositions. Possibly the dehydrating temperature employed affects the readjustment of the UH_3 lattice and thus governs both the density and the appearance of uranium as a discrete phase discernible by X-rays.

It should be noted that hydrogen atoms do not affect X-radiation and that the diffraction pattern of UH_3 is due solely to the arrangement of uranium atoms therein. Further, the low densities we observe for intermediate compositions affords evidence that the helium, used as a displacing medium, does not enter the assumed lattice vacancies.

The arrangement of points on figure (6-1) is such that one might draw a nearly straight line through the three right-hand points, and an intersecting straight line from the ordinate axis. This, if correct, would strengthen the above argument that low-temperature removal of H atoms does not greatly affect the lattice or the density. Additional points are needed to corroborate this however. This entire problem is closely connected with our theoretical studies on the nature of uranium hydride and further work is planned.



7.00 SPECIAL APPARATUS AND TECHNIQUES

The following laboratory methods and equipment are described briefly in the hope that others will find them useful. Our work required development of several anaerobic techniques and methods of gas purification which would appear to be of general utility. More detailed publications are anticipated. The microscope hot-stage has not been in service long enough to determine its range of usefulness, but it has been in operation for some weeks. It has shown an ability to withstand 150 psi internal gas pressure and to hold a vacuum of 2 microns.

7.10 Removal of Oxygen, Moisture and Acidic Gases from Nitrogen, Argon, Hydrogen and Helium.

Two convenient methods were devised for ultra-purification of inert gases. The first (E.B.D.) is simply a Drierite tower to which sodium-potassium eutectic alloy (Callery Chemical Co.) is added. The liquid alloy on shaking under inert gas spreads over the surface of the Drierite granules forming a shiny film of great surface area. This film forms best on white Drierite which has previously been exposed to air. The granules merely act as an inert substrate. Care must be taken never to expose the alloy or metallized granules to air.

The second method (T.R.P.G.) provides an oxygen-absorbing liquid of great capacity and vigor. It is prepared by adding a commercial sodium dispersion (National Distillers) to a solution of benzophenone forming the blue ketyl. The sodium dispersion is available in a variety of liquids, but nujol (mineral oil) and diphenyl ether have a desirably low vapor pressure. A mixture of one gram sodium with 4g. benzophenone in a liter of nujol or biphenyl ether yields a deep blue colloidal suspension which absorbs oxygen with great rapidity. The ultimate capacity of this mixture is roughly a liter of dry oxygen, but the practical capacity is about 500 cc. This liquid is far more effective than aqueous alkaline pyrogallol both in sensitivity and capacity. The solution is most satisfactory when used in conjunction with a sintered glass bubbler. The blue color is replaced by amber when the solution is spent. Adsorption of an ethereal ketyl solution on baked porous clay or dehydrated asbestos yields a solid whose oxygen absorbing power has not been measured.

7.20 The Tufts Drybox and Continuous Purifier (T.R.P.G.)

This drybox offers certain advantages of ruggedness and size to warrant a brief description, even though the equipment was not constructed under this contract. It has been in operation for nearly two years. The sketches given indicate the design and dimensions. The body is made from 1/16" steel, the left-hand end and bottom being 1/8" steel. All seams are welded. The lock is a section of 1 1/4" O.D. standard steel tubing brazed to the wall of the box. The doors are 1/2" steel stock with recessed rubber gaskets. The lock and doors were carefully machined to mate. Three hatch-cover wing-bolt assemblies ensure that the doors close hermetically.

The gloves are 27" neoprene size 10 type R1145 obtained from Scientific Services, Inc. Oakland, Calif. All valves are 1/8" spring-loaded plug cocks (Lunkenheimer). A pair of cocks within the drybox permit the operator to control

the inflation of the gloves at all times, to evacuate a vessel within the box or to introduce a stream of gas.

The problem of purifying the gas in the drybox was complicated by the use of both nitrogen (Linde 99-99%) and argon in the box. Thus standard purifiers for argon (Ti-Zr, Mg etc.) could not be used with nitrogen owing to nitride formation. This problem was solved by employing sodium which does not react readily with nitrogen but which removes all other reactive gases. The use of molten sodium is impractical because of the tenacious film which soon covers the surface. The simple expedient of employing a sodium electrode in a 7000 volt 200 ma spark discharge proved most successful. The assembly is shown in the figure. A spark discharge is passed between a metal rod and an alumina crucible containing an approximate 2" cube of sodium. The spark (which becomes arc-like as a column of sodium vapor forms) continuously erodes the sodium surface producing a spray of atomized metal.

The circulating system consists of a dual blower, one blower (with a filter on the inlet side) causing the gas to circulate in the drybox, the other forcing the gas (ca 10 c.f.m.) through the sodium spark and through a large filter of fiberglass. The latter prevents sodium dust from becoming a nuisance in the box. Dust from ordinary operations in the box, such as grinding, etc. is largely picked up by the filter on the second blower. Rapid circulation of gas (ca 30 c.f.m.) in the box is essential owing to the rapid diffusion of oxygen in through the gloves.

It is never necessary to change the gas in the box unless gross accidental contamination occurs. Gloves may be changed without air entering the box by use of a device which seals the inside of the glove port. This device is a rubber covered aluminum disc which is clamped against the glove port from the inside. This disc has a tube through which the new glove may be evacuated and filled with pure inert gas.

7.30 Microscope Hot-Stage for Vacuum and High Pressure Studies (T.R.P.G.)

This device was designed for the observation of the surface of uranium during hydrogen absorption or desorption. So far as is known it is the only device designed for the microscopic study of specimens at high temperature and gas pressure and as such it may be of interest in connection with various A.E.C. problems such as hydrogen corrosion, hot pressing of metals in gas or in vacuum, mechanism of sintering, studies of grain growth, etc.

The detailed design was worked out by Mr. Walter Pavelchek of Tufts following the over-all plan of the writer. At the date of this report it has been tested for tightness towards vacuum (0.1 mm) and pressure (150 psi) and is being calibrated by observation of the melting point of several metals.

The Figure 7 which is a full size drawing describes the assembly. The body is made of free-machining stainless steel. The windows of polished clear sapphire. Gaskets are silicone rubber. A chromel-alumel 28 ga. thermocouple is introduced through tube A via a Conax gland. It is lead upwards through a perfor-

ated sapphire disc (not shown) on which the specimen rests so that the thermocouple end is within 1 mm of the specimen. This specimen disc is supported on a silica tube which carries a coiled platinum filament located just below the specimen disc and heats the latter to any desired temperature. Distilled water is circulated over the top of the stage and a water-immersion objective is employed. The use of high-refractive index sapphire and water between objective and specimen permits a longer working distance than would be possible in air. At the moment an ordinary 8 mm objective is used without cooling water and no serious overheating has been observed at ca 400°C specimen temperature.

The connection D is attached to a stainless steel needle valve which in turn is attached to a 3-way stopcock permitting argon, hydrogen or vacuum to be used in the stage.

While most easily adapted to studies by transmitted light, provision has been made for vertical illumination of specimens by a rhomboidal prism located beside the objective.

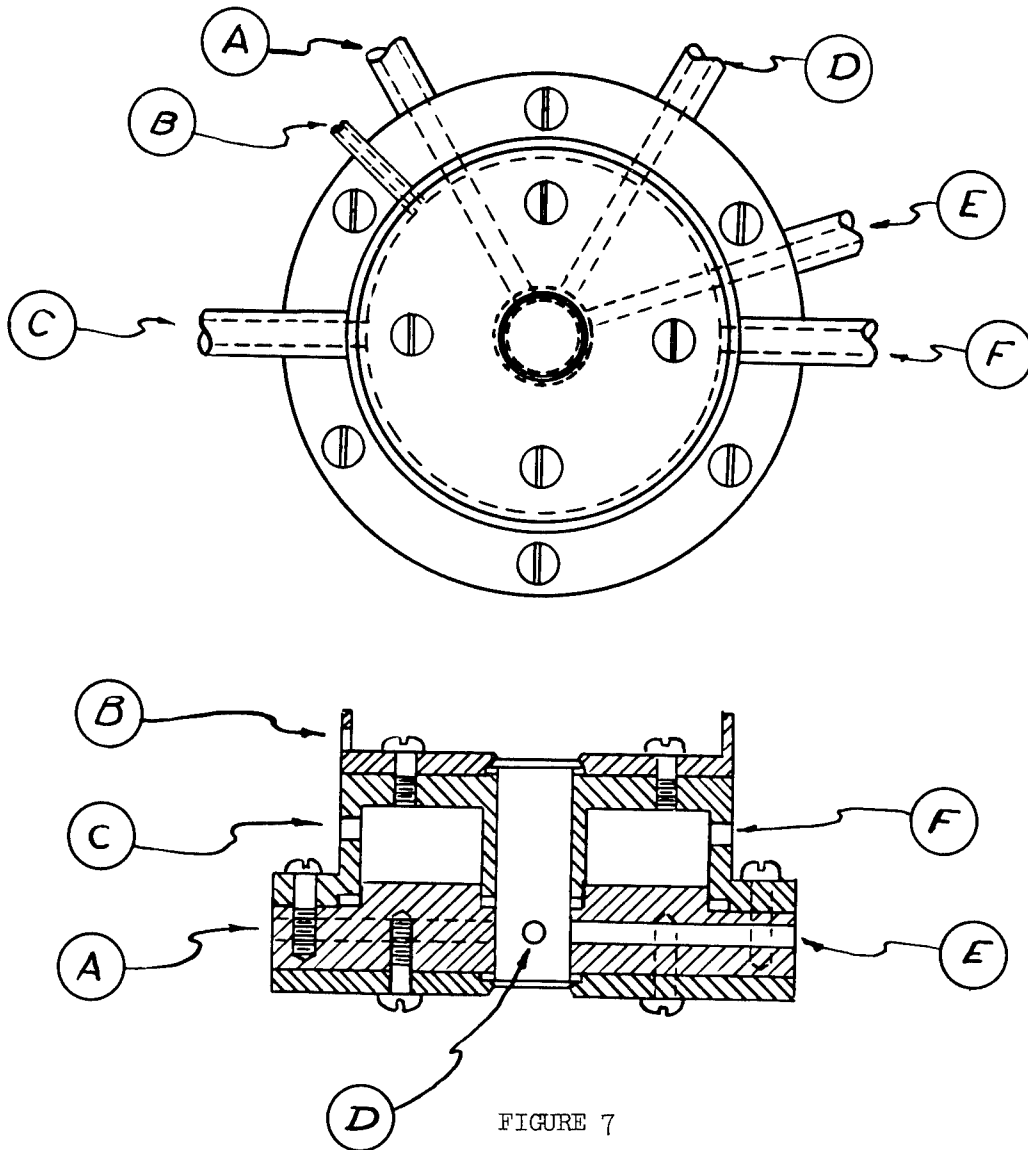


FIGURE 7

Microscope stage for high-temperature high-pressure studies (designed by Walter Pavelcheck and built by Andrew Levesque).

Scale - Full Size

Stock - Stainless steel, sapphire windows, silicone gaskets.

A Thermocouple duct
 B Water run-off tube
 C Cooling water outlet

D Vacuum and pressure connection
 E Heater lead duct
 F Cooling water inlet

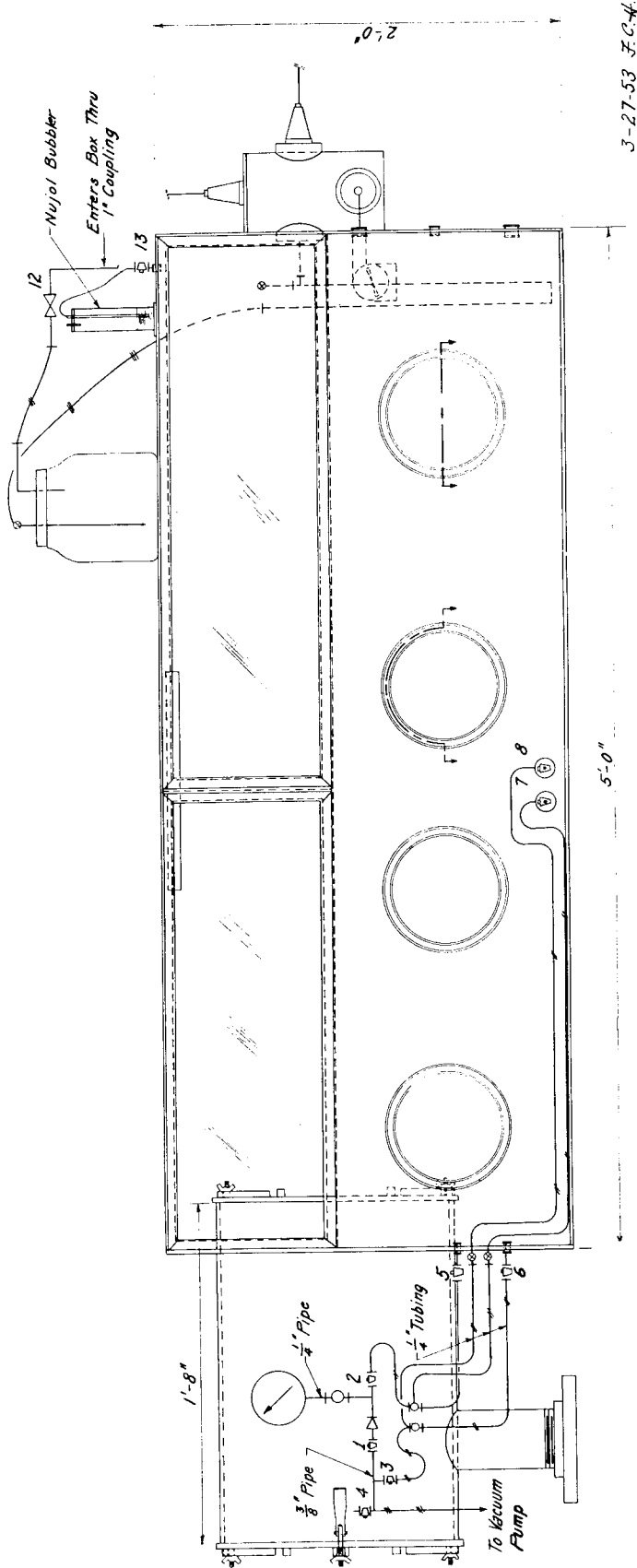


Fig. 7.1 - Tuft's Drybox. Front view. Vacuum lock on left, gas purifier on right. Cocks 1,3,4,6 are in vacuum manifold. Cocks 2,5 are in nitrogen manifold. Nitrogen line is behind cock 5.

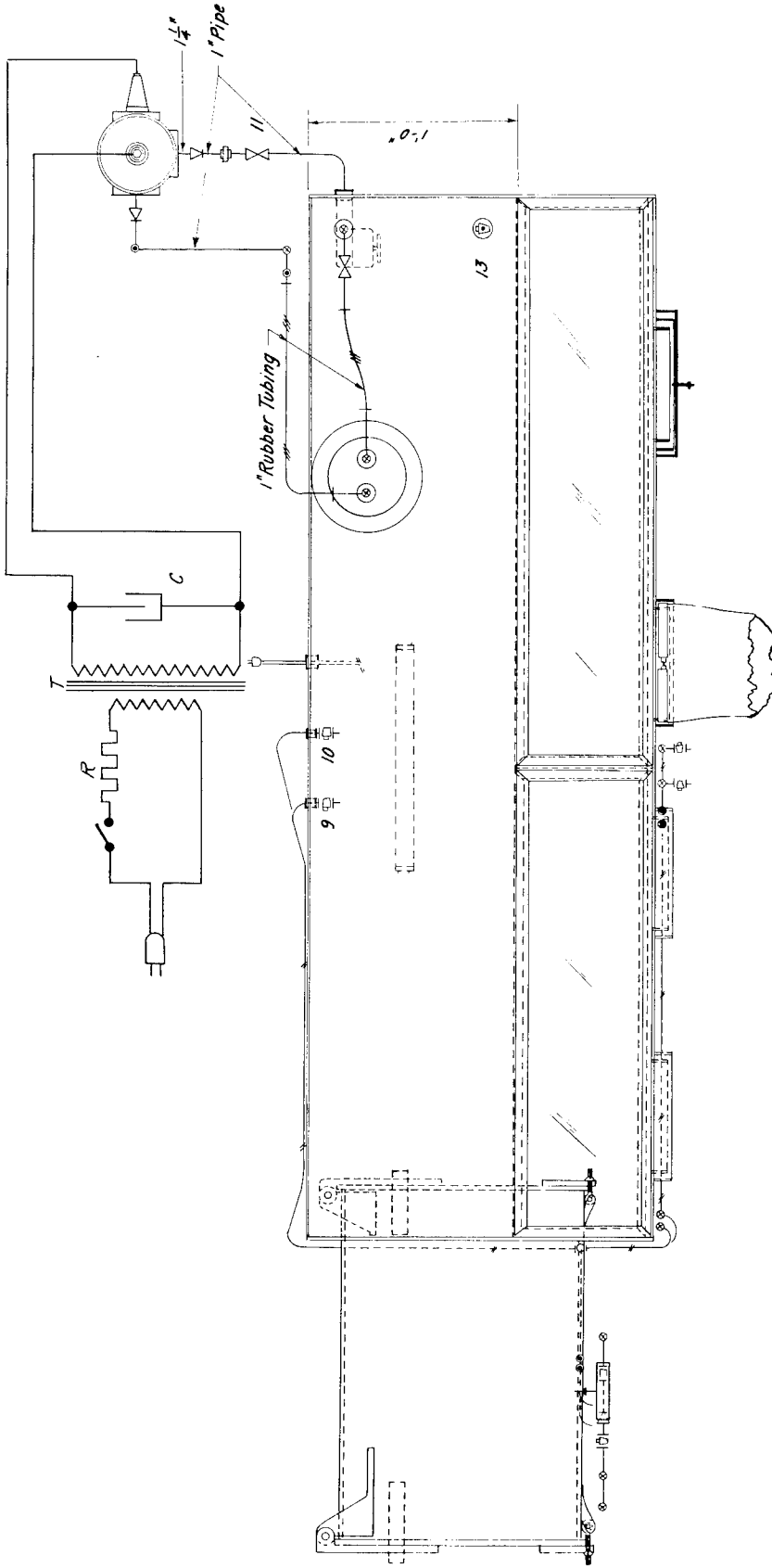


Fig. 7.2 - Tufts Drybox. Top view, showing 7000 volt transformer (top) and construction of vacuum-tight doors to vacuum-lock (left). Note double ports for gloves and outer port-seal at lower right. Cocks 9 and 10 are inside box. Cock 13 is gas outlet, connected to bubbler (not shown).

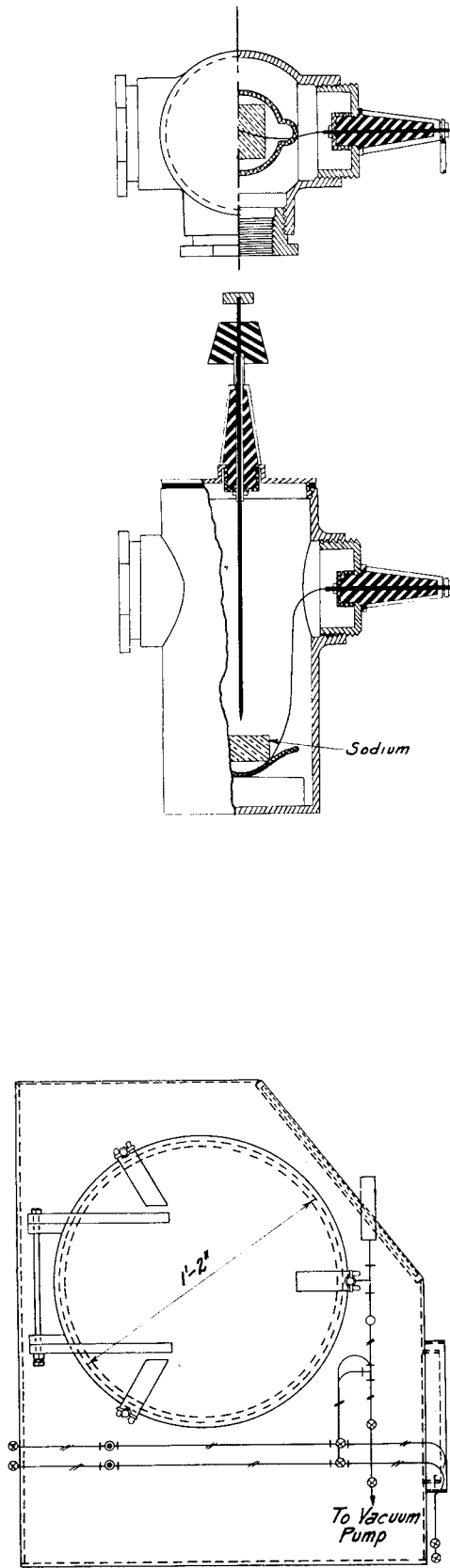


Fig. 7.3 - Details of gas purifier (upper) and view of left-hand end of drybox (lower). Three heavily cross-hatched portion of upper drawings represent porcelain insulators. Area cross-hatched in opposite direction is rubber.

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