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CHEMICAL RESEARCH: GENERAL CHEMISTRY

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REPORT FOR PERIOD OF APRIL 10 TO MAY 10, 1944

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ABSTRACTS

Problem #4

The preparation of  $UO_2Br_2$  by the controlled oxidation of  $UBr_4$  is discussed. Some oxide is formed with the  $UO_2Br_2$ . The melting point of  $UBr_4$  has been determined as  $519^\circ \pm 2^\circ C$ . The addition of 10%  $UBr_3$  lowers this greatly showing liquid solubility of  $UBr_3$  in  $UBr_4$ . The formation of solvates of  $UBr_4$  is discussed.

The melting point of  $UCl_4$  has been found at  $590^\circ C$ . This is lowered by the addition of  $UCl_3$ . Anhydrous  $UO_2Cl_2$  has been prepared by the oxidation of  $UCl_4$  and some of its properties measured. The distillation of  $UCl_4$  in  $Cl_2$  and  $Cl_2 + CCl_4$  has been studied. It is found that the composition of the product is dependent on the temperature. Only at high temperatures is an exact compound formed as a product.  $UCl_3$  has been studied. At high temperatures a disproportionation takes place, forming  $UCl_4$  and other products not yet identified.

The X-ray structure for  $UCl_4$  by Mooney (CP-1533) has been confirmed.  $UCl_3Br$  has approximately the same structure but it is no longer truly body centered.

Problem #6

The formation of  $UN_2$  has been studied at  $250^\circ C$  and  $350^\circ C$ . It is found that  $UN$  is not an intermediate. The final composition approaches  $UN_{1.75}$  at both temperatures.

The melting point of  $UN$  has been found to be  $2630^\circ C$ . Buttons of fused  $UN$  have been included in reductions of tetrabromide with calcium and iodine booster. No attack was suffered by the mononitride in the process.

Problem #12

Equipment for the study of the hydride system to 2400 p.s.i. and  $700^\circ C$  has now been obtained.

-/-/-/-/-

Abstracts follow for the work done at Ames and reported in other reports:

CC-1499 - Analytical

Problem #7

It has been found that previous attempts to analyze uranium nitrides by the Dumas method failed because of insufficient oxygen used in the combustion. Several adaptations of the regular Dumas analysis were made, the principal one of which is the use of a substantial quantity of potassium chlorate as a source of oxygen. By observing the precautions given, uranium nitrides may be analyzed with errors of less than 0.5%.

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CT-1501      Problem #10

Thermal data show that a very small amount of molybdenum in tuballoy lowers the solid transformation temperatures greatly, and that at about 5% Mo, both solid transformations are undetected, although the solidus temperature is essentially that of the melting point of the pure metal.

Evidence is on hand to show that at least one compound exists between tuballoy and magnesium although actual compositions have not been determined. X-ray studies of Mg-Tu alloys show that neither pure Tu nor Mg are present.

A hot stage for hydrogen etching of metallographic samples has been constructed, and this has been used to identify the tuballoy phase in several alloys.

Problem #11

A very few, weak diffraction maxima of what appears to be the gamma form of the metal have been obtained in a sample containing also UO. Additional evidence for UO is cited.

There is no x-ray evidence for any compound other than  $UCu_5$  in the Cu system.

The structure of the cubic compound  $USn_3$  is given. X-ray diagrams indicate two further compounds in this system.

X-ray evidence has been obtained for at least one compound in the Mg system.

Thermal data indicates that a 5% Mo alloy retains the gamma structure of the metal at room temperature. X-ray diagrams of an unannealed sample were clearly not the alpha form of the metal, but were too diffuse to determine certainly the structure of the gamma phase.

-/-/-/-/-/-

In addition a summary report on the analysis of uranium for fluorine has been substituted. An abstract follows:

CC-1502

Results for fluorine in uranium metal which have been obtained to date in other laboratories and in this laboratory were tabulated and the reasons for discarding methods used previously in this laboratory were pointed out.

A method of analyzing for fluorine in uranium metal, which entails controlled oxidation, dissolving the  $U_3O_8$  in a solution of ferric sulfate and sulfuric acid, distilling the fluorine as fluosilicic acid, and determining the fluorine in the distillate by the "back-titration" procedure of W. S. Allen, has been described in detail. Scrupulous attention to details is necessary

-4-

for the success of this method; this is, of course, true of any method for this particular analysis. The average blank, for which the results have been corrected, was  $2.2 \pm 0.6$  micrograms of fluorine per 200 ml of distillate, or  $1.3 \pm 0.4$  ppm. fluorine. The recovery of fluorine from spiked samples of pure  $U_3O_8$  has been investigated; in the range of 50 to 100 micrograms of fluorine (added as sodium fluoride), recoveries of 98 to 99 per cent have been obtained when 200 ml of distillate were collected.

Results for different samples of uranium metal (Ames) analyzed by this method varied from  $1.1 \pm 0.3$  ppm to  $13.0 \pm 1$  ppm of fluorine. The analyses of a biscuit metal yielded 3.8 ppm. fluorine; of a uranium carbide, 5.7 ppm. fluorine.

It is believed that this procedure has given correct results, within the limitations stated in the report, for the quantity of fluorine in the metal. If a more sensitive method for determining fluorine in the distillate could be developed, the procedure for oxidation and distillation might be adapted to the determination of fluorine in the product. Work will be done to adapt the procedure for use in determining fluorine in uranium bromides and chlorides.

Problem No. 4 - A. S. Newton, Associate Section Chief, Coordinator

Study of Uranium Halides and Their Properties

I. Uranium Bromides

A. UO<sub>2</sub>Br<sub>2</sub> - (J. Powell and R. Nottorf)

In an attempt to prepare pure UO<sub>2</sub>Br<sub>2</sub>, following unsuccessful attempts with Br<sub>2</sub> on UO<sub>2</sub> and UO<sub>3</sub>, (CC-1496), dry UBr<sub>4</sub> was slowly heated in a stream of O<sub>2</sub>. At about 150°C bromine was slowly evolved, and over a considerable period of time the color of the material changed from brown to red. The color appeared to be redder the more anhydrous the material, while the absorption of water vapor changed the color to yellow.

This material is essentially completely soluble in water to give a yellow solution. Analysis of the material, however, indicates that with the samples yet produced, not enough bromine is present to give the formula UO<sub>2</sub>Br<sub>2</sub>. In one sample heated at 162° for 46 hours, analysis (57.3% U; 33.7% Br) indicated about 84% UO<sub>2</sub>Br<sub>2</sub> and the rest oxide. A previous run at 170° for 25 hours analyzed 60.0% U and 29.9% Br, corresponding to 93% UO<sub>2</sub>Br<sub>2</sub>.

Higher temperatures tend to yield greater percentages of oxide. At 350°C much of the material was black in color, and this black material was insoluble in water. In a similar experiment, attempting the production of UO<sub>2</sub>Br<sub>2</sub> from UBr<sub>3</sub> and O<sub>2</sub>, the UBr<sub>3</sub> caught fire at room temperature, instead of reacting smoothly, but it is not known if this is the usual behavior. Oxygen diluted with nitrogen, or dry air, may be more satisfactory where pure O<sub>2</sub> fails.

B. Physical Properties of UBr<sub>4</sub> - (R. Nottorf, J. Power, A. Newton)

The melting point of sublimed UBr<sub>4</sub> was determined from cooling curves to be 519° ± 2°C, using a Type K potentiometer and chromel-alumel thermocouple. Addition of about 10% UBr<sub>3</sub> lowers this M.P. to 503°C, showing solubility of UBr<sub>3</sub> in liquid UBr<sub>4</sub>.

The determination of the vapor pressure curves for liquid and solid UBr<sub>4</sub> by the transpiration method is in progress. Since data are yet incomplete, the results will be presented in next month's report.

C. The Solubility Studies of Uranium Halides - (V. Calkins)

In last month's report (CC-1496) the solubility of UBr<sub>4</sub> in several organic solvents and lack of solubility in PCl<sub>3</sub> and SnCl<sub>4</sub> were reported. The unsuccessful attempts to recover UBr<sub>4</sub> from the solvents in which it was soluble lessened the value of quantitative results, and the ever-produced solvates suggested that the study of these and their decomposition would indicate the value of the solvents more completely than data on how much halide could dissolve in, or react with, 100 g of solvent.

Procedure: With slight variations, the procedure for these studies was to treat solid halide in a dry atmosphere with solvent, observing color change of undissolved salt and solution. When sufficient time for solution had elapsed, the undissolved salt was filtered from the solution and the undissolved solid evacuated to remove solvent and analyzed. The solution was taken to a residue, either under a vacuum, or under a stream of inert carrier gas. A minimum of heat was applied. This material also was analyzed. Since it was always found to be a solvate, attempts at removal of the solvent were made, using high vacuum and gradually increasing heat, and checking the progress visually and analytically.

Attempts were made to salt out the uranium halide from organic solution by passing in dry HBr, but without success. In the several cases in which a crystalline precipitate occurred, it was apparently an HBr salt of the solvent, (e.g. with dioxane perhaps  $C_4H_8O_2 \cdot 2HBr$ ; with methyl cyanide  $CH_3CN \cdot HBr$ , etc.).

Results: The results of these studies parallel those reported for  $UBr_4$  in the previous report (CC-1496). The tri and tetra-bromides and chlorides were insoluble in  $PCl_3$  and  $SnCl_4$  in hydrocarbons, and in non-polar organic compounds. Normally no color change is produced on the anhydrous halide crystals by these solvents; the green emulsion-like product produced on  $UCl_3$  by  $PCl_3$  being an exception.

The polar solvents usually produce an immediate color change upon the uranium halides, and this is apparently a result of solvation, e.g.,  $UBr_4$  is red-brown, but solutions are usually green.  $UCl_4$  is less soluble than  $UBr_4$ , and the tri-halides still less soluble in most organic solvents.

All attempts to free  $UBr_4$  from the solvation of dioxane, pyridine, diethyl ether, and acetonitrile have been unsuccessful; the U-Br bond itself is apparently ruptured or replaced by U-O or U-N or U-C before the solvent can be completely removed. It appears doubtful that organic solvents will be useful in this manner for the purification of  $UBr_4$ .

## II. Uranium Chlorides

### A. Thermal Studies on $UCl_4$ and a $UCl_3-UCl_4$ Mixture - (T. Butler and A. Newton)

The L-ray Group have obtained a powder-type diagram in their x-ray studies of a single crystal of  $UCl_4$ . The single crystals of  $UCl_4$  are prepared at about  $400^\circ$ , and the fact that a powder diagram is obtained may indicate that a crystal transformation has taken place on cooling. Heating and cooling curves have been taken to check this and to check the melting point of pure  $UCl_4$ .

The apparatus consisted of a quartz tube to hold the melt, a quartz-jacketed chromel-alumel thermocouple dipping into the melt, and a Wheelco Potentiometer. An atmosphere of purified helium was kept over the  $UCl_4$  at all times during the experiment. Fifty grams of pure  $UCl_4$  were used. In general, the heating curve was less reliable than the cooling curve. In the second experiment, 6 grams of  $UCl_{3.09}$  were added and another series of heating and cooling curves taken. The region of the sharp break in the curve is tabulated below:

Curve	$UCl_4$		$UCl_4 + UCl_3$	
	Thermal Arrest	Average	Thermal Arrest	Average
Heating	574-579°C	576.5°C ± 2.5°C	536-542°C	539°C ± 3°
Cooling	588-593°C	590.5°C ± 2.5°C	574-579°C	576.5°C ± 2.5°

It is to be noted that from the cooling curve on pure  $UCl_4$ , the melting point is 590.5°C ± 2.5. This agrees well with the value of 588°C ± 5, as reported by Kraus (N-117). The data obtained gave no indications of any other break in the curve to indicate a crystal transformation, but unless it were quite large it would not be detected with the method of measurement used.

The lowering of the melting point of pure  $UCl_4$  by 14°C by the addition of about 10%  $UCl_3$  indicates a miscibility of the two compounds in the liquid state. This does not agree with the phase studies on  $UCl_4$  of Kraus (N-117).

#### B. Preparation and Properties of Anhydrous $UO_2Cl_2$ - (O. Johnson)

An attempt to prepare  $UO_2Cl_2$  by the reaction between  $UO_3$  and  $Cl_2$  gave no reaction up to 400°C and the reaction between  $UO_3$  and  $Cl_2$  gave  $U_3O_8$  at 400°C.

It was subsequently found that when oxygen gas was passed over anhydrous  $UCl_4$  in a glass reaction tube, a reaction took place at 300-350°C to give a fine yellow powder. It dissolved completely in  $H_2O$  to give a yellow solution. The following analysis was obtained: 69.50% U and 21.00% Cl. (Theory for  $UO_2Cl_2$ ; 20.8% Cl, 69.9% U). Considering the remaining 9.5% to be oxygen, this corresponds nearly to  $UO_2Cl_2$ . The product tends to sinter during the reaction and in pulverizing the products a small unreacted portion of  $UCl_4$  was found at the center of a lump of  $UO_2Cl_2$ . The sintering can be prevented by agitating the reacting tube during the reaction.

The yellow  $UO_2Cl_2$  is very hygroscopic.  $UO_2Cl_2$  is insoluble in  $CCl_4$ , xylene and benzene. It is insoluble in, but reacts with, ethers and chloroform. It is soluble in alcohols, acetophenone, pyridine and dioxane, but reacts with all of them.

Mixtures of  $UCl_5$  and  $UCl_6$  also react with oxygen to give  $UO_2Cl_2$ . In this case there is the intermediate step of the conversion to  $UCl_4$ .  $UCl_3$  begins to react with  $O_2$  at about  $150^\circ$ . It probably goes to  $UO_2Cl_2$ , but in the experiment performed there was some unconverted chloride left and a small amount of oxide present in the product. The oxide may have formed in the initial stages of the reaction when considerable heat developed. This could be remedied by diluting the  $O_2$  with an inert gas, but the use of  $UCl_4$  and  $O_2$  appears to be the best method of preparing  $UO_2Cl_2$ .

C. Sublimation of the Higher Chlorides of Uranium at Various Temperatures - (O. Johnson and T. Butler)

When  $Cl_2$  is passed over heated  $UCl_4$ , higher chlorides of uranium (above  $UCl_4$ ) sublime to the cooler portions of the apparatus. These sublimes have been studied in connection with the purification of  $UCl_4$  by subliming these chlorides and subsequently reconverting them to  $UCl_4$ . The reaction of  $Cl_2$  and  $UCl_4$  is also of interest as a possible direct method of preparing  $UCl_5$  and  $UCl_6$ :

Previous experiments were carried out by passing a stream of  $Cl_2$  gas over powdered  $UCl_4$  in a pyrex reaction tube and collecting the sublimate in a cool 500 cc round bottom flask. The present experiment was carried out in a similar apparatus and sublimate fractions at various temperatures were collected. The rate of flow of  $Cl_2$  gas was maintained at about 10 cc/minute throughout the experiment. The composition of the sublimate and the temperature at which it was sublimed are given in the table below. Unnumbered entries are from previous individual experiments in slightly different apparatus.

<u>Sublimate Fraction</u>	<u>Temperature <math>^\circ C</math></u>	<u>Composition (Cl/U ratio)</u>
1	300-310	4.7
2	390	5.22
-	420	5.34
3	460	5.65
4	525	4.98
5	550-560	4.56
-	560	4.58
-	600	4.0
-	630	3.98

It is immediately evident that  $UCl_5$  is not formed over any appreciable temperature range. It appears that under the conditions of the experiment, the sublimate is always a mixture of chlorides.

To test the effect of rate of  $Cl_2$  gas flow, two experiments with a rate of  $Cl_2$  flow of 200 cc/minute at 430 and  $440^\circ C$  were carried out. The sublimate analyzed  $UCl_{5.25}$  and  $UCl_{5.29}$ , respectively. This indicates little or no effect of rate of flow of  $Cl_2$ .



Introduction of  $\text{CCl}_4$  vapor into the  $\text{Cl}_2$  stream also produced little effect. At  $440^\circ$  the sublimate in this case analyzed  $\text{UCl}_5.42$ . The only difference observed was that there was no residue in the reaction tube. There usually is a small amount of yellow crystals ( $\text{UO}_3$  or  $\text{UO}_2\text{Cl}_2$ ) remaining.

It is to be noted that the California group describe a production method (S-51) for  $\text{UCl}_5$  by passing  $\text{Cl}_2$  plus  $\text{CCl}_4$  vapor ( $p = 1/2^\circ$ ) over  $\text{UCl}_4$  heated to  $650^\circ$  at a rate of 10/liters/minute.

We have obtained a considerable quantity of  $\text{UCl}_5$  as prepared by Dr. Kraus' group by the reaction of  $\text{UO}_3$  and  $\text{CCl}_4$ . The product is crystalline and black with some brown material; it analyzed as  $\text{UCl}_5.97$ . A density determination by displacement of benzene gives the density value of 3.81. The mixtures of chlorides obtained in the reaction of  $\text{Cl}_2$  on  $\text{UCl}_5$  are always fine brown powders which are much more difficult to handle than Kraus' product.

#### D. Properties of $\text{UCl}_3$ - (T. Butler)

In view of the fact that it is difficult to reduce large quantities of  $\text{UCl}_4$  completely without special apparatus, a quantity of  $\text{UCl}_3$  for experimental purposes has been made by passing  $\text{HCl}$  through heated  $\text{UH}_3$  in an upright pyrex tube. Some purification is accomplished by passing the  $\text{HCl}$  through a small tube of heated hydride before it enters the main reaction tube.

At room temperature  $\text{UCl}_3$  is olive green in color. It becomes red-dish brown at about  $300^\circ\text{C}$  and around  $450^\circ\text{C}$  it is a dark purple color. It returns to the olive green color on cooling to room temperature.

The product prepared by this reaction of  $\text{HCl}$  and  $\text{UH}_3$  analyzed  $\text{UCl}_3.11$ . When it was heated to  $150^\circ\text{C}$  considerable gas was evolved. Apparently  $\text{HCl}$  gas is adsorbed by the solid  $\text{UCl}_3$  and is held very strongly.

When  $\text{UCl}_3$  is heated at  $850^\circ\text{C}$  in vacuum, there appears to be considerable thermal decomposition. The quartz tube has sublimate in bands of varying colors. A considerable amount of material analyzing  $\text{UCl}_4$  sublimed just above the furnace. The residue and other portions of sublimate have not been analyzed yet. This decomposition has been previously discussed in California Report S-156 in connection with an attempt to estimate vapor pressures of  $\text{UCl}_3$ .

#### E. X-ray Studies on $\text{UCl}_4$ and $\text{UCl}_3\text{Br}$ - (N. Baenziger and R. E. Rundle)

Last month the lattices of  $\text{UCl}_4$  and ( $\text{UCl}_3\text{Br}$ ) were reported as probably tetragonal. This has been confirmed, and the structure recently reported by R. Mooney (CP-1533) has also been verified. Our values for the lattice spacings are seen to be in good agreement with Mooney's.

Mooney

$$a_0 = 8.295 \pm 0.010 \text{ \AA}$$

$$8.296 \pm 0.009$$

$$c_0 = 7.480 \pm 0.010 \text{ \AA}$$

$$7.487 \pm 0.009$$

$$\rho = 4.87 \text{ g/cc}$$

( $\text{UCl}_3\text{Br}$ ) is tetragonal with the lattice constants.

$$a_0 = 8.434 \pm 0.010 \text{ \AA}$$

$$c_0 = 7.690 \pm 0.010 \text{ \AA}$$

$$\rho = 5.12 \text{ calc. as } \text{UCl}_3\text{Br}$$

$\text{UCl}_3\text{Br}$  was prepared by Harf's group by the reaction of  $\text{UCl}_3$  and  $\text{Br}_2$ , but their chemical analysis of the product is in better agreement with a formula  $\text{U}_2\text{Cl}_5\text{Br}_3$ , and the increase in the unit cell size over that of  $\text{UCl}_4$  is in better agreement with this further replacement of Cl by Br. On this basis  $\rho = 5.39 \text{ g/cc}$ .

$\text{UCl}_4$  is body centered, but extra, faint lines appear in the mixed halide which indicate that the lattice is no longer truly body centered. The replacement of Cl by Br in the  $\text{UCl}_4$  lattice is not, therefore, a random replacement. In view of the somewhat uncertain formula of the mixed halide the structure has not been investigated further.

Area Problem No. 6 - A. S. Newton, Associate Section Chief, Coordinator

I. Preparation of Uranium Nitride - E. Tucker and P. Figard

The reaction of  $\text{UH}_3$  with  $\text{N}_2$  has been studied at  $250^\circ\text{C}$  and  $350^\circ\text{C}$ . A plot of the N-U ratio vs. time shows no break at one N/U, indicating that there is no change in reactivity of  $\text{UH}_3$  over metal or hydride. If a product  $\text{UN}$  is obtained by this reaction, it is only by accidentally stopping the reaction at the right time. The curves, Figure 1, show that at both temperatures the limiting ratio of N-U is about 1.75, a result in agreement with previous findings at higher temperatures.

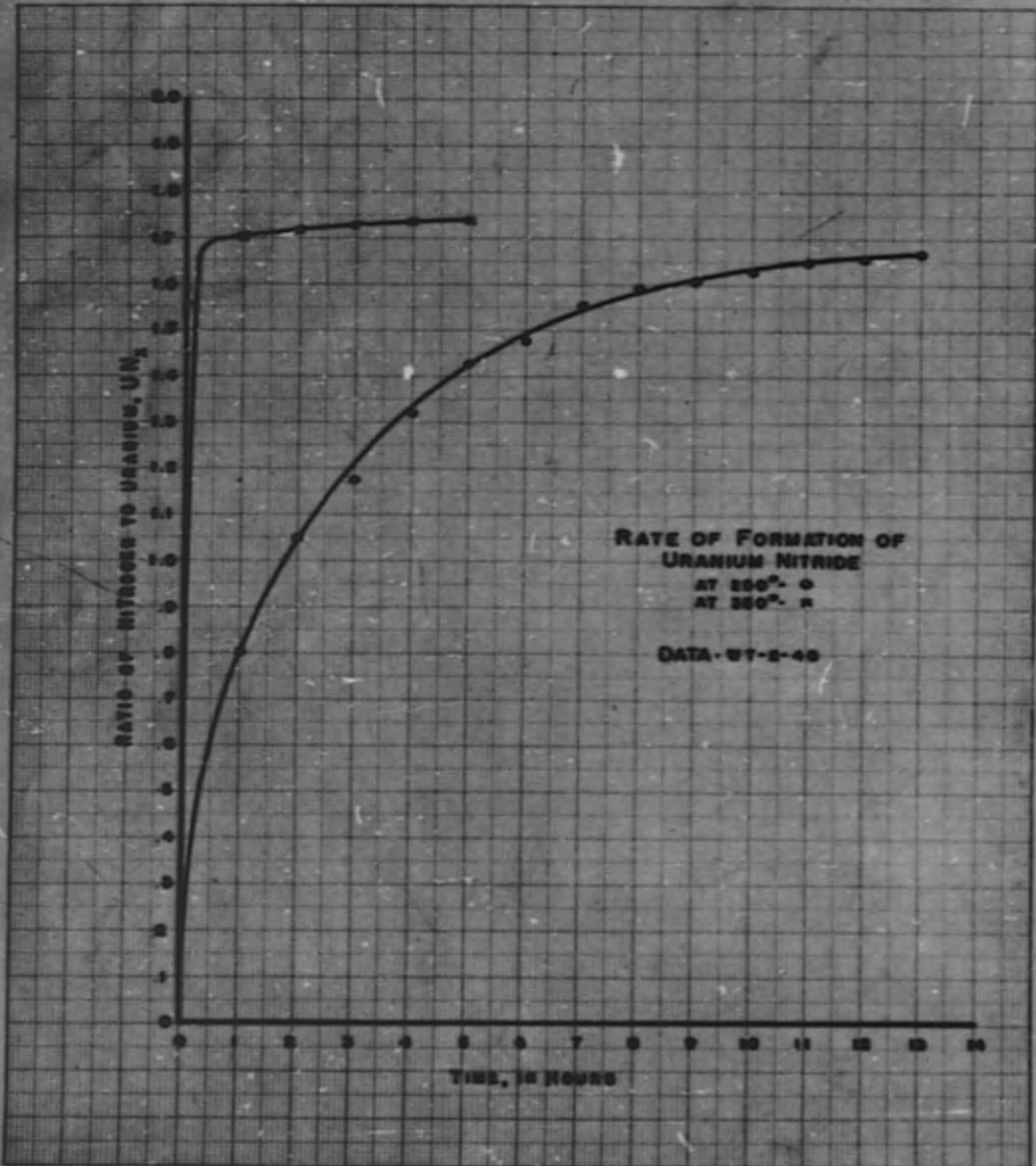
Studies on the reaction of chloride with ammonia to form nitride have yielded the following results to date. At  $300^\circ\text{C}$   $\text{UCl}_4$  is reduced to  $\text{UCl}_3$ . Ammonium chloride is a product. If the product is cooled in ammonia a light green powder is formed which contains several moles of  $\text{NH}_3$  per mole  $\text{UCl}_3$ . Flushing with  $\text{N}_2$  or He, eliminates most of the ammonia. The product at  $300^\circ\text{C}$  in this case contains very little nitrogen and no nitride is formed. At  $750^\circ\text{C}$  the reaction goes much further. A reduction in chloride content from 37% for  $\text{UCl}_4$  to about 4% for the product was obtained. No satisfactory nitrogen analyses on the product have been obtained.

RATIO OF NITROGEN TO URANIUM,  $UN_2$

RATE OF FORMATION OF  
URANIUM NITRIDE  
AT 250°- O  
AT 250°- R

DATA-WT-2-48

TIME, IN HOURS



ACCEPTED BY ENGINEER, A. V. NO. 100018  
RESEARCH, U.S. ARMY, WASHINGTON, D.C.

II. Uranium Mononitride - A. Daane, N. Carlson and A. Wilson

In preparing some small fused mononitride buttons by heating mononitride powder in an atomic hydrogen arc, the melting point of this material, as measured by an optical pyrometer, was observed to be  $2630^{\circ}\text{C} \pm 50^{\circ}\text{C}$ .

Two of these fused mononitride buttons were given to Dr. Keller's group to be tested for corrosion resistance in a reduction bomb. The first button was placed in the bottom of a bomb charge of calcium, tuballoy tetrabromide and iodine. The sample was not corroded to a detectable extent, although it appeared to be somewhat more brittle than before due to thermal strain.

The other button was placed in the center of a bomb charge of calcium, uranium tetrabromide and iodine. This button was trapped in the biscuit, and metallographic examination showed no appreciable attack by the reduction.

Area Problem No. 12 - A. S. Newton, Associate Section Chief, Coordinator

Study of Hydride at High Pressures

An apparatus for working with hydride at pressures up to 2400 p.s.i. and to about  $700^{\circ}\text{C}$  has been completed. Results on the study in this range should be obtained in the coming months.

**END**