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UNITED STATES ATOMIC ENERGY COMMISSION

MELTING POINT—COMPOSITION DIAGRAMS
IN THE U-UBr₃ SYSTEM

By
Carl Thurmond

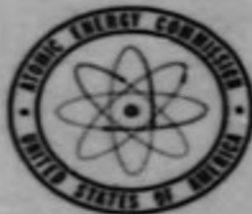
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ABSTRACT

A portion of the liquid-solid phase equilibrium region of the system U- U-UBr_3 has been investigated by the method of thermal analysis.

Uranium tribromide was prepared by introducing bromine vapor into a bulb containing finely divided uranium formed from the hydride. Cooling curves were obtained with the tribromide and then with various compositions of tribromide and uranium.

The information obtained showed that no solid subhalide exists but that the metal was soluble in the halide.

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MELTING POINT—COMPOSITION DIAGRAMS IN THE U-UBr₃ SYSTEM

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INTRODUCTION

Work reported by Webster in CK-671 and CK-873 indicated a considerable solubility of uranium metal in uranium tribromide and the possible existence of lower oxidation states of uranium. In order to get further evidence concerning this system, the liquid-solid phase equilibrium between uranium and uranium tribromide has been investigated by the method of thermal analysis. Melts of various compositions of the metal and halide were made up and cooling curves run. From the information obtained from these curves it was possible to construct a temperature composition diagram for this system.

PROCEDURE

Uranium tribromide was prepared by the vacuum distillation of a stoichiometric quantity of freshly distilled bromine into a bulb containing finely divided uranium made from the hydride. This bulb was then sealed from the rest of the system and heated about 15 hours at temperatures between 550 and 600°C. The tribromide was removed from the bulb in a carbon dioxide atmosphere and transferred to carbon dioxide filled, waxed rubber stoppered bottles. The analysis of the first preparation of halide gave 2.98 ± 0.01 as the ratio of mols of bromine to mols of uranium.

Cooling curves with the tribromide were obtained by putting about 50 grams of the salt into a porcelain crucible contained in a side armed

quartz tube and heating in a resistance furnace. Chromel-alumel (and later, Pt-Pt, 10%Rh) thermocouples were used, protected from the melt by a small porcelain protection tube. The apparatus was arranged in such a way that the thermocouple protection tube was held up out of the melt while heating and could be lowered into the melt when the right temperature was reached. The quartz tube was connected to a vac line, flushed 3 or 4 times with purified helium and the heating and cooling of the melt done under slightly better than an atmosphere of the gas.

The composition of the melt was changed by administering small weighed pellets of uranium through a tube into the melt in such a manner that no air was admitted. This allowed one to add the metal to the hot melt. To insure a rapid approach to equilibrium, stirring was accomplished by strapping a tungsten rod with a loop at right angles to it at the end, to the protection tube and by rapidly raising and lowering the protection tube, the melt could be agitated.

The porcelain crucibles were attached to some extent by the melt, leaving a thin black coating on the inside. After using these for a number of cooling curves a change was made to molybdenum crucibles. The subsequent cooling curves showed no detectable difference but these crucibles withstood the action of mixtures of salt and metal much better. The porcelain protection tubes were used throughout but were not attacked as much as the porcelain crucibles as they were kept out of the melt except for intermittent stirring and during the running of the cooling curve.

DISCUSSION

When cooling curves were obtained with the first preparation of tribromide, it was found that the melting point rose gradually with continued heating and was accompanied by condensation of uranium tetrabromide on the cooler portions of the quartz tube. A maximum temperature about 15°C above the initial melting point was reached in 5 or 6 hours of heating above the melting point. Analysis of the melt with this maximum melting point gave Br/U as 2.93. Addition of metal to this produced a lowering in melting point of about 10°C. by the time the composition had changed to 2.8, and further additions of metal produced no appreciable change of melting point. The possibility that this initial rise in melting point was due to the formation of a solid solution was dismissed when X-ray analysis of the maximum melting temperature

melt failed to disclose any difference between it and the uranium tribromide.

A new preparation of the tribromide was made as before in which the sealed bulb was heated at 550 to 600°C. for about twice as long as in the previous preparation. The transfer of the salt from the bulb to stoppered bottles was again accomplished under an atmosphere of carbon dioxide but was done much more rapidly than before. The analysis of this preparation gave 3.01 ± 0.01 for Br/U. Cooling curves obtained with this gave a melting point at the maximum melting point of the previous melt, although there was still some formation of tetrabromide. Additions of metal to this melt produced a lowering in melting point of approximately the same amount as with the other tribromide when metal was added to it.

It was found that if the maximum temperature reached in equilibrating the mixtures before running a cooling curve was around 900°C., no more metal would go into the solution than that required to give a Br/U ratio of around 2.5. One series of cooling curves in which enough metal was present to give a composition of less than 2 for Br/U if all the metal reacted, was equilibrated at temperatures in excess of 1050°C. The first curve obtained gave what appeared to be a slight "break" in the cooling curve plot at a temperature of about 880°C. as well as the long arrest at the temperature of the melting point of the eutectic. The melt was heated back up to better than 1050°C. and held there for about an hour with intermittent stirring. The cooling curve obtained after this, showed a slight "break" at around 950°C. as well as the usual long arrest at the lower temperature. Two more curves were run with heating and stirring as before, the first giving a slight "break" at about 1000°C. and the second, one at 1020°C. However, as other cooling curves showed "breaks" in them of this same order of magnitude in temperature ranges where it was quite certain nothing should happen, it is felt that this set of results is not adequate evidence of the location or existence of the equilibrium line. The melt when examined after the last curve showed that enough metal had dissolved to give a composition less than Br/U of 2.

CONCLUSIONS

The rise in melting point of the first preparation of tribromide

upon continuous reheating is believed to be due to the distillation of tetrabromide from the melt which was there as an impurity. It did not show up in the analyses because stoichiometric amounts of bromine and uranium had been originally put together, and if an impurity of oxygen had been present during this reaction, it would have reacted with the uranium thus leaving an excess of bromine which would give some tetrabromide. Also, in the handling of the tribromide in the carbon dioxide atmosphere some moisture might have been picked up and tetrabromide and oxide might result in the subsequent heating. As the uranium analyses were made by dissolving the samples in a nitric acid solution the Br/U ratio would be left unchanged.

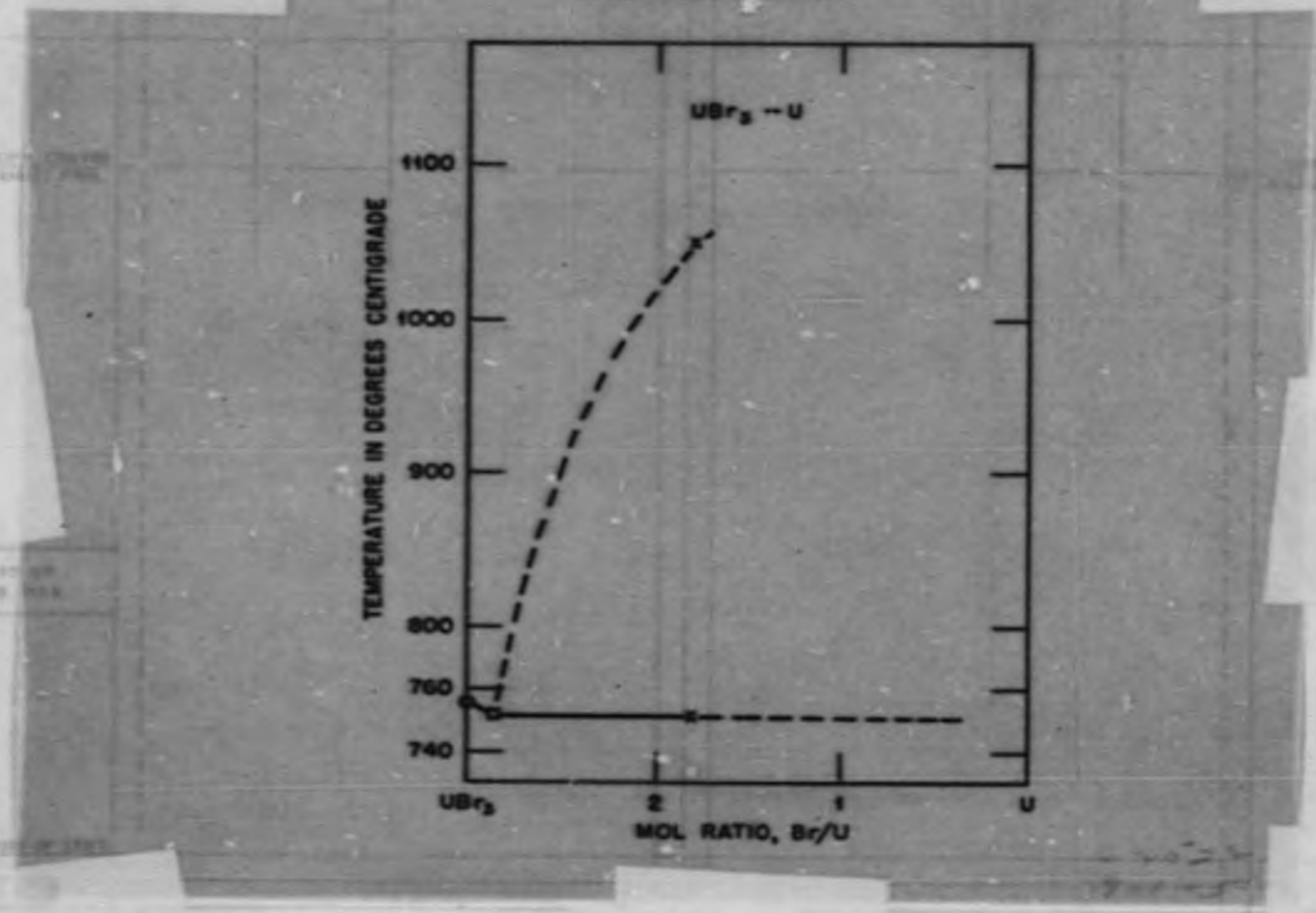
From the data obtained, the best value for the eutectic composition seems to be between Br/U of 2.9 and 2.85, or in terms of mol fraction of tribromide, between .97 and .95.

A series of cooling curves were mentioned above for which the equilibrating temperature was in excess of 1050°C. These curves all showed an arrest of about the same duration at approximately the temperature of the eutectic melting point. These results would disprove the existence of a stable plus two oxidation state of uranium because, if such did exist, the length of the arrests at the eutectic melting point temperature would steadily decrease then disappear as the composition approached Br/U of 2. Furthermore, if the composition during the last curve of this series was less than or equal to Br/U of 2, it would be impossible for a stable plus two bromide to exist in the light of the results shown by the curve.

The accompanying figure shows a few representative cooling curves and a plot of the temperature-composition diagram which best fits the observed results.

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