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**THE REACTION OF FERRIC CHLORIDE
WITH URANIUM TETRACHLORIDE**

ABSTRACT

Solid ferric chloride reacts with solid uranium tetrachloride to form a complex iron-uranium chloride compound at approximately 263° . The vapor pressure of this compound is nearer to that of uranium tetrachloride than to the vapor pressure of ferric chloride.

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**Oak Ridge, Tennessee
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716-1

THE REACTION OF FERRIC CHLORIDE

WITH URANIUM TETRACHLORIDE

INTRODUCTION

The occurrence of false J's together with the frequent presence of appreciable amounts of iron in charge material has led to the investigation of the possible formation of a compound containing both uranium and iron and having a vapor pressure greater than that of either uranium tetrachloride or ferric chloride. The presence of such a compound especially if its iron to uranium ratio were high could conceivably account for false J occurrence. In addition, the presence of an iron-uranium compound with a lower vapor pressure than that of FeCl_3 would also be of interest due to the frequent purification of UCl_4 from iron by sublimation of the tetrachloride.

Since the iron in charge material normally occurs as ferric chloride this investigation was confined to a study of the interaction of the anhydrous forms of solid ferric chloride and solid uranium tetrachloride.

EXPERIMENTAL

Initial experiments consisted of observing visually the results obtained by gently heating a mixture of FeCl_3 and UCl_4 under N_2 in a pyrex tube by means of a bunsen burner. When a certain point in the heating operation was reached the greenish black mixture changed abruptly to a buff-colored material, indicating that some type of chemical reaction

716-2

had ensued. Upon further heating, the buff-colored material decomposed, forming a green melt and volatile FeCl_3 which condensed in the cooler portions of the tube.

A mixture of UCl_4 and FeCl_3 corresponding to a molar ratio of 1 U to 4 Fe was placed in a pyrex tube and heated under vacuum in an electric furnace, the temperature being measured by use of a chromel alumel thermocouple and a Brown recording potentiometer. A plateau in the heating curve was obtained at 263°C . and on cooling the buff-colored compound was found to have formed. In a second run in which the heating was stopped at a temperature slightly less than 263°C . the buff material had not been formed, thus establishing the fact that the occurrence of the plateau was concurrent with the formation of the buff-colored compound.

Using the recording potentiometer, mixtures of UCl_4 and FeCl_3 varying in initial molar ratio of Fe/U from approximately 1/5 to 5/1 were heated and the temperature at which the compound formed was found to be essentially constant at 263°C . regardless of the initial ratio of Fe/U. Some of this buff-colored compound was prepared under vacuum using excess FeCl_3 and after formation was held between 260 and 285°C . for three hours to allow the excess FeCl_3 to distill out of the compound. Chemical analysis of this material gave us the empirical formula $\text{U}_7\text{FeCl}_{28}$. A vapor pressure run by the transpiration method was made at 440°C . on some of the compound prepared in this manner and it was found that decomposition takes place at this temperature.

Another portion of the compound, prepared as stated above, was placed in a porcelain boat inside a quartz tube and heated under N_2 gas

716-3

by means of an electric tube furnace. Some buff material together with FeCl_3 distilled at approximately 320°C . collecting on the walls of the cooler portion of the tube. The FeCl_3 became predominant and some of the material in the boat had turned dark green at 350°C . indicating that some decomposition was taking place. Evidence of decomposition increased with temperature and a green melt was formed at 550°C . which contained only 0.5% Fe by chemical analysis and had a Cl/U ratio of 4.5.

Another portion of the compound, prepared in the manner previously described, was heated in a pyrex tube under vacuum by means of an electric furnace. The buff material began to distill by 400°C . and evidence of decomposition was noted at 440°C . Decomposition became vigorous and a portion of the material exploded at 550°C . On further heating vigorous decomposition could be seen and by 675° all of the materials had volatilized. During this run the material in the hot zone remained buff-colored indicating that both decomposition products volatilized as soon as formed.

CONCLUSIONS

From these experiments it is evident that a compound of U, Fe and Cl was formed when UCl_4 and FeCl_3 were heated together. The compound formed at 263°C . and had a vapor pressure between that of FeCl_3 and UCl_4 . It decomposed before its melting point was reached and decomposition became quite violent at approximately 550°C . in vacuum. Decomposition yields UCl_4 and a volatile Fe compound (presumably FeCl_3).

Since the compound is not formed until 263°C . and has no appreciable vapor pressure until a temperature of 320 to ~~400~~⁴⁵⁰ is reached, it can not

716-4

readily account for the large percentage of false J's which occur below 300°C. This coupled with the fact that little correlation has been found between the iron content of charge material and false J occurrence would seem to indicate that this compound could not account for any appreciable percentage of the false J's.

Purification of UCl_4 from FeCl_3 by sublimation would obviously be complicated by the formation of this compound during sublimation since this iron-uranium compound has a vapor pressure much nearer to that of UCl_4 than FeCl_3 . On heating under H_2 at atmospheric pressure, 0.5% Fe remained in the melt formed at 550°C. On heating in vacuo the compound did not decompose until a temperature was reached such that both decomposition products (UCl_4 and FeCl_3) volatilized almost immediately.

Temperatures where the vapor pressure of the compound becomes appreciable or where decomposition takes place readily are near the temperature where UCl_4 sublimates. Ferric chloride has a vapor pressure of 35.5 mm. at 256°C., so that removal of the FeCl_3 by holding the temperature slightly below 263° for some time would be preferred rather than allowing the compound to form and then attempting to decompose it or sublime it away from the UCl_4 .

716-5

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716-6