

Preparation of Anhydrous Uranium Tetrachloride and Measurements on Its Magnetic Susceptibility

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The reaction of UO_2 with CCl_4 vapor was carried out in a vacuum of 10^{-5} mmHg at 500°C in order to prepare UCl_4 of high purity. The lattice parameters were calculated from X-ray analysis to be $a_0=8.278\pm 0.002$, $c_0=7.460\pm 0.009$. The product thus obtained was verified by chemical and X-ray analyses to be of anhydride form. The magnetic susceptibility was measured over the temperature range from liquid N_2 to liquid He temperature, which revealed a deviation from the straight $1/\chi-T$ relation toward lower temperature.

I. INTRODUCTION

In the U-Cl system, there are known to exist four compounds, UCl_3 , UCl_4 , UCl_5 and UCl_6 . Their chemical, physical and thermodynamic properties have been extensively investigated⁽¹⁾⁽²⁾ as well as those of the fluorides. Among these compounds UCl_4 is used as the starting material for the synthesis of various uranous complexes, for its high solubility in many organic polar solvents such as methanol, ethanol, acetone, as reported by Selbin *et al.*⁽³⁾⁽⁵⁾ and Bagnall *et al.*⁽⁶⁾ This compound is also used as the starting material for the preparation of $\text{UC}^{(7)}$, UN , US_2 ⁽¹⁾⁽⁸⁾, USe_2 ⁽¹⁾ *etc.* for its high reactivity. It is subjected to sol-gel treatment in the form of hydrochloric acid solution, from which UO_2 crystal with high purity can be prepared. The high vapor pressure of UCl_4 at relatively low temperature suggests that it should be useful for non-aqueous reprocessing of spent fuel. The physical properties of UCl_4 are shown in Table 1, together with the results of X-ray analysis measured by Staritzky⁽⁹⁾.

However, UCl_4 is so hygroscopic as to be deliquescent with a partial pressure of anything more than 2 mmHg of water vapor in the atmosphere, and thus a dry box is always needed for its handling. Concerning ThCl_4 , which is also very hygroscopic, it has been reported that its tetragonal symmetric crystal, which is the form most commonly encountered and which is isomorphous with UCl_4 has been found to be really a hydrated compound,

and that the anhydrous compound had orthorhombic symmetry. Since the same morphology may also exist for the chloride also, the UCl_4 is required to be of high purity.

Table 1 Physical properties of UCl_4

Crystal structure	Body centered tetragonal (ditetragonal-dipyramidal)
Space group	$I4/amd (D_{2d}^{19})$
Lattice parameters†	$a_0=8.298\pm 0.001 \text{ \AA}$ $c_0=7.486\pm 0.001 \text{ \AA}$
Density	4.894 g/cc (X-ray)
Melting point	$590^\circ\pm 1^\circ\text{C}$
Boiling point	792°C
Vapor pressure:	
Solidous	$\log P \text{ mmHg} = -10,427/T + 13.2995$
Liquidous	$\log P \text{ mmHg} = -7,205/T + 9.65$

† Results of X-ray analysis of UCl_4 have been reported in detail by R.C.L. Mooney⁽¹⁰⁾.

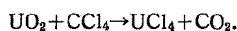
Two distinct methods are available for preparing UCl_4 :

- (1) Gas phase reaction in which the vapor of a chlorinating reagent such as HCl , Cl_2 , CCl_4 , SOCl_2 is made to react with uranium oxide at elevated temperature;
- (2) Liquid phase reaction in which uranium oxide at lower temperature is refluxed with a halogenating reagent such as CCl_4 , $\text{CCl}_2=\text{CClCCl}_3$ (hexachloropropene) or CCl_3CCl_3 (hexachloroethane). In labo-

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ratory scale, the most common method utilizes the reaction between UO_3 and hexachloropropene.

In this study, in order to obtain UCl_4 with high purity, the former principle was adopted: *i.e.*, the reaction between UO_2 and UCl_4 at high temperature. The principal reaction is



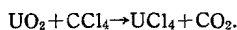
This method has the advantage that impurities are not introduced from the outside of system, and also that control of the amount of the higher chlorides is possible by applying suitable conditions. The purity of the product can be raised by repeated sublimation and precipitation.

As a representative property of UCl_4 thus prepared, we measured the magnetic susceptibility down to liquid He temperature to extend the data obtained by Bommer⁽¹²⁾, Dawson⁽¹³⁾ and Stoenner *et al.*⁽¹⁴⁾, who only measured down to liquid N_2 temperature.

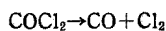
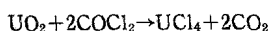
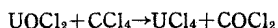
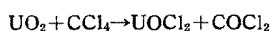
II. EXPERIMENTAL

The mechanism of the reaction of UO_2 with CCl_4 vapor is described elsewhere⁽¹⁾ in detail.

The principal reaction is



The competitive reactions are:



Besides, at $100^\circ \sim 175^\circ\text{C}$ in high vacuum, UCl_5 undergoes a disproportionation reaction:



And at about 170°C , UCl_6 decomposes into UCl_4 and Cl_2 :



Taking these circumstances into account, the preparation of UCl_4 was carried out as described below.

1. Materials

The UO_2 was supplied by Sumitomo Metal Mining Co. Ltd. The O/U ratio was 2.02, and spectrometric analysis revealed the im-

purities to be: C<15, N<30, F<10, Mg 4, Al 40, Si<50, Cl<10, Ca<10, Cr 10, Fe 10, Ni 10, Cu 4, Mo<3, Ca 0.3, Sn 3, Pb 3, in ppm. Spectrograde CCl_4 by E. Merck was used.

2. Preparation

The apparatus for the reaction is shown in Fig. 1. In the quartz reaction tube inserted in the furnace are arranged end to end four sections of quartz tube each about 10 cm long, which serve to collect individual fractions of the deposited products. The end section is closed at its extremity and it carries a quartz boat containing about 2 g of UO_2 sample. During the reaction the temperature is usually kept higher in the furnace A (500°C) than in B (200°C). The glass ampoule in the bulge E of the reaction tube contains liquid CCl_4 , previously distilled and trapped at solid CO_2 temperature, and packed in 10^{-3} mmHg of vacuum. The magnetic hammer is padded with teflon sheet. When the vacuum reached about 10^{-5} mmHg and the temperature of the sample attained 500°C , the cock F was closed, and the reaction between UO_2 and CCl_4 was initiated by breaking the glass ampoule with the magnetic hammer, and gently heating the bulge in order to promote the vaporization of CCl_4 . As soon as UCl_4 was formed by reaction, it immediately sublimed on account of its high vapor pressure of 0.64 mmHg at 500°C , and deposited on the wall of the section of tube next to that carrying the boat. It took about 4 hr to complete the reaction, *i.e.* to entirely consume the UO_2 in the boat. While the reaction was incomplete, an intermediate product UOCl_2 remained in

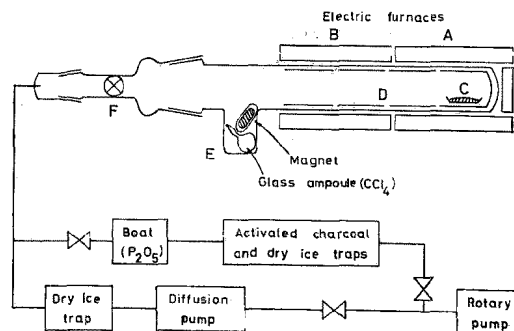


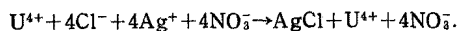
Fig. 1 Apparatus for reaction and vacuum sublimation

the boat, which was confirmed by X-ray analysis. The UCl_4 crystals thus obtained had a blackish-violet color at high temperature, but which turned dark green at room temperature. When the furnace B was kept somewhat cooler, *i.e.* $100^\circ\sim 150^\circ C$, a reddish-brown colored UCl_3 crystallized on the lower temperature sections, as well as the UCl_6 , of blackish green color. The UCl_6 was analyzed by thermogravimetry, which revealed that Cl_2 was released by decomposition at about $170^\circ C$. After the reaction tube was cooled, it was evacuated to remove reaction gases such as $COCl_2$ and residue CCl_4 , then it was filled with Ar gas. The cock F was again closed and the reaction tube was separated and brought into a dry box which was previously filled with Ar gas and dried with P_2O_5 powder. The dry box was constantly swept with Ar gas during the handling of the product. In certain runs the process was recycled, the UCl_4 thus obtained being again sublimed in the same apparatus for recrystallization on the wall in vacuum.

3. Analysis

The uranium content of the UCl_4 was determined by the gravimetric analysis, using what is known as the ammonia method⁽¹⁶⁾. After all the uranous ion was oxidized to uranyl ion by the addition of dilute nitric acid, ammonia was added to the solution, then the precipitate of ammonium diuranate was filtered, dried and ignited. The ash, U_3O_8 , was weighed, and its content confirmed by X-ray analysis.

The chlorine content of UCl_4 was determined by potentiometric titration, using a $AgNO_3$ standard solution. This reaction is



The silver electrode potential

$$E = E_0 + 0.059 \log[Ag^+]$$

Thus, if an excessive amount of $AgNO_3$ solution is titrated, the electrode potential will sharply increase with rising concentration of Ag^+ ion. The equivalent point was determined from the dE/dV curve. A saturated calomel electrode was used as reference electrode and the salt bridge was filled with saturated potassium sulfate. The result of

analysis is as follows:

Found U: 61.6 ± 0.2 , Cl: 38.1 ± 0.1 , Total: 99.7%

Calculated U: 62.66, Cl: 37.34%

This data reveals that the UCl_4 obtained was anhydrous, which agrees with the result of X-ray analysis. Contamination by higher chlorides was also exceedingly low. No marked difference in analytical data were seen between the recycled and non-recycled products. The X-ray analyses were carried out by powder camera on samples enclosed in a glass capillary in a dry box, and by diffractometry on samples covered with polyvinyl chloride sheet.

4. Susceptibility Measurement

Measurements of susceptibility on the UCl_4 were made by the Faraday method over the temperature range of $4.2\sim 80 K$ in a field of about 10 koe. The temperature was measured with both a Au-Co/Cu thermocouple and carbon resistance. A recycled sample was chosen. It was sealed in a glass tube filled with He gas. After the measurement on the sample, the glass tube without the samples was blank tested down to 4.2 K in order to correct the result of measurement. The susceptibility did not vary over a range of magnetic field between 2 and 11.6 koe, which indicated that no ferromagnetic impurities were present in the sample. The values of magnetic susceptibility thus obtained were also corrected for the diamagnetism⁽¹⁸⁾ caused by the completely filled cores, adopting values of 22.9×10^{-6} for Cl^- and 31.5×10^{-6} for $U(IV)$.

III. RESULTS AND DISCUSSION

1. X-ray Analysis

Powder diffraction data for UCl_4 are shown in Table 2, along with those of Staritzky⁽⁹⁾. The lattice constants were calculated from the data in the high angle range and were found to differ slightly from those obtained by Mooney and Staritzky from the data in the lower angles.

$$a_0 = 8.728 \pm 0.002$$

$$c_0 = 7.460 \pm 0.009$$

The diffraction data in the lower angles well agreed with those by Staritzky and also

Table 2 Powder diffraction data for UCl_4

Present work			Staritzky	
hkl	$d_{\text{obsd.}}(\text{\AA})$	I	$d_{\text{obsd.}}(\text{\AA})$	I/I_0
101	5.54	VS	5.53	100
200	4.14	S	4.12	45
211	3.32	M	3.30	35
112	3.15	M	3.14	50
220			2.92	10
202	2.77	W	2.77	20
301	2.59	S	2.58	70
103	2.380	VS	2.385	65
321	2.193	M	2.191	45
312	2.143	S	2.137	85
400	2.068	M	2.064	50
213				
411	1.940	VW	1.939	25
004	1.852	W	1.862	50
420	1.815	VW	1.847	35
303				
402				
332	1.732	VW	1.730	30
204	1.708	VW	1.703	20
323	1.686	VVW	1.690	5
422				
501, 431	1.617	VW	1.620	30
224	1.576	VW	1.576	25

VS: very strong, S: strong, M: medium, W: weak, VW: very weak, VVW: very very weak

with those by Mooney, on a UCl_4 sample enclosed in capillary in a dry box. The recycled and non-recycled specimens yielded identical X-ray patterns. No lines belonging to other chlorides such as UCl_3 , UCl_5 , UCl_6 and UOCl_2 were observed. In the present study UCl_4 was prepared in high vacuum and handled within a dry box. The result of chemical analysis also showed that the product obtained was anhydrous UCl_4 . Therefore, it may be concluded that UCl_4 , which was reported by Mooney and Staritzky to belong to body centered tetragonal symmetry is anhydrous, in contrast to the case of ThCl_4 , for which the anhydrous phase is orthorhombic and the hydrate, tetragonal. As for the hydrated UCl_4 , Chretien has reported⁽¹⁴⁾ diffraction data on $\text{UCl}_4 \cdot 9\text{H}_2\text{O}$, and which differ entirely from that of the anhydrate. Thus, according to these results the existence of an

unknown new phase of anhydrous UCl_4 could hardly be considered.

2. Magnetic Susceptibility

The results of the measurements are presented in Fig. 2 together with Dawson's data, indicated by the dashed line. It is seen that the extrapolation of the present result towards higher temperatures well agrees with Dawson's, while a deviation from the straight $1/\chi - T$ relation occurred at about 50 K, resulting in a finite value at 0 K. Such a deviation from the Curie-Weiss law is also seen in the case of nickelocene⁽¹⁷⁾ with its susceptibility-temperature curve breaking away at 20°K, as also with $\text{U}(\text{SO}_4)_2 \cdot 4.22\text{H}_2\text{O}$ (break away point 50 K)⁽¹⁸⁾, and with lanthanide complexes having an even number of electrons around the central ion, such as $\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{Eu}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ⁽¹⁹⁾. In these complexes the deviation from the Curie-Weiss law has been understood to originate from zero-field splitting between the singlet ground state and the lowest excited state larger than kT . For nickelocene the zero-field splitting was estimated to be 25.6 cm^{-1} from its magnetic susceptibility extrapolated towards 0 K. Another evidence of the large zero-field splitting has been provided by the absence of signals in ESR measurements for nickelocene and

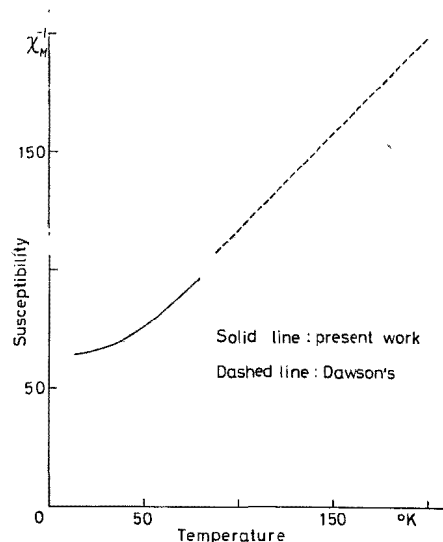


Fig. 2 Temperature dependence of inverse molar susceptibility

$\text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. Ghosh carried out ESR measurements on UCl_4 specimen from 90 K to room temperature⁽²⁰⁾, but no signals due to paramagnetic resonance were observed. Thus, neglecting the relaxation broadening, the absence of ESR signals together with the foregoing susceptibility behavior would lead to the conclusion that the ground state of UCl_4 is also singlet, and that the zero-field splitting between the ground state and the lowest excited state would be considerable, as in the examples given above of certain lanthanide complexes and others.

For UCl_4 , each uranium atom is surrounded by eight chlorine atoms in which four chlorines form a flattened tetrahedron and the other four, an elongated one, thus forming a distorted dodecahedron with a point symmetry around D_{2c}^{20} . A similar distorted dodecahedron with symmetry around $\text{U}(\text{IV})$ is attributed to the case of uranium doped in ZrSiO_4 and that of the uranium in U_3P_4 . In the former case, based on assignments for the absorption spectrum made by Richman *et al.*⁽²¹⁾, it has been suggested that the ground state of $\text{U}(\text{IV})$ was singlet with the lowest excited state located 155 cm^{-1} above. In order to explain the high-temperature susceptibility of U_3P_4 , it was assumed⁽²²⁾ that the ground state of $\text{U}(\text{IV})$ was singlet with the lowest excited state located 8.9 cm^{-1} above. Thus, for UCl_4 with the same symmetry as the foregoing examples, it can also be considered that the ground state is singlet and that the lowest excited state is at a level where the interaction with the ground singlet can be neglected up to about 50 K. However it not yet clear how the symmetry around $\text{U}(\text{IV})$ is related to the state of the ground level.

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