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Final Report

MASS SPECTROMETRIC STUDY OF THE MOLECULAR SPECIES FORMED
DURING VAPORIZATION OF UCl_4 in Cl_2 AND $AlCl_3$

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ABSTRACT

Solid UCl_4 was heated in a graphite effusion cell, and the species that vaporized in vacuum and in the presence of Cl_2 and AlCl_3 were investigated by mass spectrometry. In vacuum, the vapor species formed was UCl_4 . The observed vapor pressure of UCl_4 was in general agreement with the literature, but the temperature coefficient was different. In Cl_2 , the molecule U_2Cl_{10} was identified from its mass spectrum and its behavior while the Cl_2 pressure was varied. That molecule had been reported by Gruen and McBeth. A new vapor species, UCl_5 , was also identified. In AlCl_3 the molecular species $\text{UCl}_4\text{AlCl}_3$ was identified from the mass spectrum and the dependence on AlCl_3 pressure. That molecule was different from the $\text{UCl}_4\text{Al}_2\text{Cl}_6$ observed by Gruen and McBeth. In the presence of Cl_2 plus AlCl_3 the molecular species $\text{UCl}_5\text{AlCl}_3$ was found in accord with results by Gruen and McBeth.

Expressions for the partial pressures of the uranium-containing vapor species are given as a function of pressures of Cl_2 and AlCl_3 in the presence of solid UCl_4 .

INTRODUCTION

A possible approach for increasing the volatility of uranium compounds to be used in laser isotope separation processes involves the formation of a stable mixed-molecular vapor species in the presence of a suitable complexing agent. One such complexing agent, aluminum trichloride, is known to form stable mixed gaseous molecules with other metal chlorides¹ and to increase the metal chloride volatility significantly. Gruen and McBeth² have reported spectrophotometric studies of gaseous complexes of UCl_4 and UCl_5 with AlCl_3 , but the composition of the complexes was not determined directly. The objective of the studies reported here was to identify by mass spectrometry the volatile products of the reaction of UCl_4 with Cl_2 and AlCl_3 , and to obtain information about the reaction thermodynamics so that the abundances of gaseous products can be estimated for various conditions of interest. It should be recognized that, within the funds and time span allotted for the present study, only the highlights of the U-Al-Cl chemistry could be covered.

More detailed studies will be required for a complete thermochemical treatment of the system.

EXPERIMENTAL

All measurements were made with a 60° sector, 12-inch-radius direction-focusing mass spectrometer equipped with a Nier-type electron impact ion source and a Knudsen cell molecular source. The instrument and the experimental technique have been described previously.³ For the present studies, a graphite effusion cell and gas inlet tube were used. With this arrangement, gaseous Cl_2 and/or AlCl_3 could be admitted to the base of the cell from an external reservoir; gas flow rates and pressures within the cell were controlled with variable leak valves. A sample of solid UCl_4 was placed in the main chamber of the cell. Temperature was monitored with a Pt, Pt-Rh thermocouple attached to the base of the cell.

To minimize hydrolysis of the UCl_4 sample during transfer operations, the sample cup was loaded in a dry box, and a stream of dry helium was flushed through the cell as the effusion source assembly was transferred to the mass spectrometer. The presence of some residual water in the sample was evident from HCl^+ and H_2O^+ peaks observed in early stages of the experiments. However, these peaks tailed off rapidly with time, and the UCl_4^+ signals were quite reproducible with time and temperature, indicating that extensive hydrolysis had not occurred. There was no evidence of interaction between the UCl_4 sample and the graphite cell.

The sample of UCl_4 used in all measurements was obtained from Dr. R. G. Bedford of Lawrence Livermore Laboratory. A preliminary mass scan of the effusing vapor at 657 K, before any reactive gases were admitted to the cell, showed the presence of a substantial fluorine

impurity in the UCl_4 . This impurity showed up in the vapor as UFCl_3 and, to a lesser extent, UF_2Cl_2 . It is estimated that the magnitude of the UFCl_3 partial pressure was about 5 percent that of UCl_4 . The effect of the fluorine impurity on the activity of UCl_4 is not known, but for the present work this effect was assumed to be negligible.

The AlCl_3 sample was prepared by vacuum distillation of Baker's Reagent Grade material, which was distilled into a glass bulb attached to the gas inlet tube. The glass bulb and its transfer line were heated as necessary to provide the desired flow of AlCl_3 into the effusion cell. Matheson "Ultra High Purity" chlorine was used.

RESULTS

Identification of Vapor Species

Components of the effusion cell beam were identified primarily from the masses, isotopic spectra, and appearance potentials (APs) of the ions formed by electron impact on the beam species. All reported ion species showed isotopic spectra in close agreement with calculated spectra for naturally occurring isotopes. Threshold appearance potentials were measured for a number of the ions by the vanishing current method, as shown in Table 1. Assignment of the neutral precursors is relatively straight-forward. In particular, the magnitudes of the APs of UCl_4^+ and UCl_5^+ are about what one would expect for the molecular ionization potentials, and offer convincing evidence for the presence of UCl_4 and UCl_5 . Other U-containing ions with APs of 12 eV or higher are clearly fragment ions. Additional evidence of species identity was obtained from the Cl_2 and AlCl_3 pressure-dependence studies described below.

Calculation of Pressures From Ion Intensities

For some species, it was possible to evaluate neutral partial pressures from the measured ion signals via the relation

$$P = \frac{KT(\Sigma I^+)}{\sigma}$$

where K is an instrument sensitivity constant, T the Kelvin Temperature, ΣI^+ the total ion yield from the neutral, and σ the total ionization cross section for electron impact. K was determined from calibrations

Table 1

ION APPEARANCE POTENTIALS*

<u>Ion</u>	<u>UCl₄</u>	<u>UCl₄ + Cl₂</u>	<u>UCl₄ + AlCl₃</u>	<u>Neutral</u>
UCl ₃ ⁺	12.0		12.0	UCl ₄
UCl ₄ ⁺	10.5	10.5	10.5	UCl ₄
UFCl ₂ ⁺	12.0			UFCl ₃
UFCl ₃ ⁺	10.5			UFCl ₃
UCl ₅ ⁺		10.7		UCl ₅
U ₂ Cl ₈ ⁺		12.0		U ₂ Cl ₁₀
Cl ₂ ⁺		12.0		Cl ₂
UCl ₃ AlCl ₃ ⁺			12.8	UCl ₄ AlCl ₃
AlCl ₂ ⁺			13.0	AlCl ₃
AlCl ₃ ⁺			12.0	AlCl ₃

*Accuracy ± 0.5 eV

with O_2 and Xe, and was found to be in agreement with previous evaluations. The σ values were estimated from the atomic cross sections of Mann,⁴ assuming additivity. Approximate fragmentation patterns were determined for UCl_2 , UCl_3 , Cl_2 and $AlCl_3$. UCl_4^+ at 12.5 eV was taken as a measure of UCl_4 abundance to avoid the fragmentation contribution from UCl_5 at 20 eV; a correction was then applied to the 12.5 eV signal to normalize to 20 eV, based on data obtained in the absence of UCl_5 . Cl_2^+ was also measured at low energy in some instances, and a similar correction was applied. Conversely, the mixed halide dimers were measured at 50 eV to gain additional sensitivity, but were corrected to 20 eV in the equilibrium calculations.

It is believed that electron impact fragmentation may be extensive for the mixed dimers, and perhaps for U_2Cl_{10} , based on previous mass spectrometric studies. Within the present study, however, it was not possible to obtain fragmentation patterns for the larger molecules; therefore, the tabulated ion yields and pressures are really lower limits, as discussed below. A molecule such as UCl_4AlCl_3 would be expected to yield abundant fragments such as UCl_3^+ , $AlCl_2^+$, and perhaps other lighter ions, all of which are also produced from other neutral progenitors present in the gas mixture. From a careful study of intensity ratios in the presence and absence of the reactive gases, however, it should be possible in future studies to ascertain the dimer fragmentation behavior.

Vapor Species Equilibria

Vapor Pressure of UCl_4

The ion intensity of UCl_4^+ , arising from the UCl_4 sample when there was no added Cl_2 or $AlCl_3$ gas, was presumed to be representative of the vapor pressure of solid UCl_4 . The data obtained and the calculated pressures of UCl_4 are given in Table 2 and presented graphically as open circles in Figure 1.

Table 2
VAPOR PRESSURE OF UCl_4

Temperature		I (UCl_4) at 20 eV	Log P(atm)
$^{\circ}\text{K}$	$\frac{10^3}{T}$		
594	1.684	4	-6.87
654	1.529	63	-5.63
627	1.595	20	-6.14
575	1.739	1	-7.5

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FIGURE 1 VAPOR PRESSURE OF UCl₄

Full line from Reference (5). Points represent present data.

Literature information on the vapor pressures of UCl_4 is not in good accord for different sources. Reference 5 has chosen one set of data as most reliable, and those results are shown as a full line in Figure 1. The present results are in fair agreement with these values, although the slope of the present data is smaller. One factor affecting our results may be the fluorine impurity in the sample noted above. Other factors probably contributed, including the possibility that the literature values were not very reliable. A careful redetermination of the vapor pressure of solid UCl_4 would be worthwhile in view of the unclear situation of the literature.

Effect of Chlorine Alone

When chlorine was passed through the cell, the ions UCl_3^+ and U_2Cl_8^+ appeared, as well as a number of others of smaller intensity, which were not further investigated. The observed ion intensities at several different temperatures and pressures of Cl_2 are reported in Table 3. The UCl_4^+ ion was measured at 12.5 eV (2 eV above threshold) to eliminate the fragment arising from UCl_5 or other complex molecules.

The results were analyzed to determine what neutral parent molecules were present in the molecular beam issuing from the effusion cell. From the ionization efficiency results given above, it was concluded that UCl_4^+ formed at 12.5 eV could only arise from neutral UCl_4 , and so the partial pressure of UCl_4 was calculated from that signal. The UCl_5^+ signal at 20 eV could have come from UCl_5 or UCl_6 . From experiments h, i, and j in Table 3, it can be shown that the neutral precursor must have been UCl_5 . In those experiments the chlorine pressure was varied over a 100-fold range while other parameters were constant, and the equilibrium constant for the reaction to produce UCl_5 was constant

[illegible][illegible][illegible]

within 10% (see equilibrium 1 of Table 3), while that to produce UCl_6 ranged over a factor of 10. Experiments f and g are also more consistent with UCl_5 than UCl_6 . The measured appearance potential of UCl_5^+ , 10.7 eV, is an equally strong indication that the ion arises from UCl_5 alone; the ionization efficiency curve of UCl_5^+ gave no indication of fragment contribution at higher energies.

The ion fragmentation pattern of UCl_5 was determined so that the pressures of UCl_5 calculated are probably accurate within a factor of two. The same comment applies to the pressures of Cl_2 and UCl_4 ; therefore, it is reasonable to use the results to derive the free energy change for the reaction:

$$\Delta G^\circ(690 \text{ K}) = -3600 \text{ cal/mole.}$$

It is not worthwhile to attempt to derive an enthalpy change from the temperature coefficient because of the scatter of the data and the question of temperature gradients. There is no literature information on UCl_5 gas. Indeed, an important result of the present study is the identification of that molecule in the vapor.

The ion species U_2Cl_8^+ can be shown to be derived from U_2Cl_{10} and not from U_2Cl_9 or U_2Cl_8 . In experiments a, b, and c (Table 3), the chlorine pressure varied over a fourfold range with other variables maintained constant. The equilibrium constant to form U_2Cl_{10} (Equilibrium 3) varied by a factor of 1.4 while that for U_2Cl_9 varied by a factor of 2 and that for U_2Cl_8 by a factor of 4. In experiments f and g, the species U_2Cl_{10} also shows better agreement in the equilibrium constant than U_2Cl_9 or U_2Cl_8 . Thus, the neutral precursor of U_2Cl_8^+ is U_2Cl_{10} .

The molecule U_2Cl_{10} was also observed by Gruen and McBeth.² We do not have information on the fragmentation of U_2Cl_{10} under electron impact, so that only a quantity proportional to the pressure can be calculated directly; however, comparison with the results of Reference 2 allows a pressure to be derived (see below).

Effect of $AlCl_3$

When $AlCl_3$ was passed through the cell, the ion $AlCl_2^+$ was taken as representative of the $AlCl_3$ pressure. The complex ion $UCl_3AlCl_3^-$ was observed in the vapor, along with a much weaker $UCl_4AlCl_3^+$ signal. The results are given in Table 4. The change in the $UCl_3AlCl_3^-$ intensity as a function of $AlCl_3$ pressure was determined at two different temperatures, and the results indicated that the neutral parent molecule was UCl_4AlCl_3 and not $UCl_4Al_2Cl_6$. In particular, in experiments c, d, and e (Table 4) the $AlCl_3$ pressure was varied over a tenfold range and the equilibrium constant for UCl_4AlCl_3 formation (equilibrium I) was constant within 10%, while that for $UCl_4Al_2Cl_6$ varied by a factor of 10. The results of experiments a and b are also in better accord with UCl_4AlCl_3 . It was not possible to vary the UCl_4 pressure because the system was saturated with UCl_4 ; therefore we did not obtain corroboration that there was only one U in the neutral parent. However, no ion with two uranium atoms and one aluminum was observed. The neutral parent molecule was then taken to be UCl_4AlCl_3 , in accord with the observation of a weak parent ion signal, as noted above.

Gruen and McBeth² found that under the conditions of their study (pressures of Cl_2 and $AlCl_3$ in excess of one atm) the results indicated the molecule $UCl_4Al_2Cl_6$ was the important species. At the low pressures of Cl_2 and $AlCl_3$ used in the present work, that species

Table 4

VAPORIZATION OF UCl_4 IN AlCl_3

Ion	Electron Energy eV	Measured Intensities					Parent Molecule	Log Pressures (atm) Calculated				
		at 681 K		621 K				a	b	c	d	e
		a	b	c	d	e						
UCl ₄ ⁺	12.5	4.2	7.2	0.36	0.39	0.45	UCl ₄	-5.48	-5.25	-6.60	-6.55	-6.49
AlCl ₂ ⁺	20	200	400	830	330	72	AlCl ₃	-5.20	-4.89	-4.62	-5.03	-5.70
UCl ₃ AlCl ₃ ⁺	50	0.36	0.9	.66	.27	.07	UCl ₄ AlCl ₃	-9.37	-8.96	-9.14	-9.54	-10.12

Equilibria

Log of Equilibrium Quotients

(1) $\text{UCl}_4 + \text{AlCl}_3 = \text{UCl}_3\text{AlCl}_3$	1.32	1.18	2.08	2.04	2.08
(2) $\text{UCl}_4 + 2 \text{AlCl}_3 = \text{UCl}_4\text{Al}_2\text{Cl}_6$	5.12	6.07	6.70	7.07	7.77

Footnote: The $\log P(\text{UCl}_3\text{AlCl}_3)$ values and the $\log$ (equil.quotients) involving it should all have an additive constant, q' , to take account of fragmentation. We shall assume that q' has the same value as q'' (Table 5).

would be destabilized to a much larger extent than $\text{UCl}_4\text{AlCl}_3$. Therefore, there is no inconsistency between Gruen and McBeth's observation of $\text{UCl}_4\text{Al}_2\text{Cl}_6$ at high pressures and our observation of $\text{UCl}_4\text{AlCl}_3$ at low pressures of AlCl_3 .

Combined Effect of Cl_2 and AlCl_3

With both Cl_2 and AlCl_3 present in the system, a new molecule ion, $\text{UCl}_4\text{AlCl}_3^+$, was observed in addition to the ones reported above. The neutral parent was $\text{UCl}_5\text{AlCl}_3$ and not $\text{U}_2\text{Cl}_{10}\text{AlCl}_3$ or $\text{UCl}_5\text{Al}_2\text{Cl}_6$, as seen from the constancy of its equilibrium constant. The results are presented in Table 5. In experiments b, c, and d, the Cl_2 pressure changed over a 10-fold range and the equilibrium constant for $\text{UCl}_5\text{AlCl}_3$ varied by 35%, while that for $\text{U}_2\text{Cl}_{10}\text{AlCl}_3$ varied by a factor of 27. In experiments a and b, the AlCl_3 pressure varied by 4-fold, and the constant for $\text{UCl}_5\text{AlCl}_3$ varied by 26%, while that for $\text{UCl}_5\text{Al}_2\text{Cl}_6$ varied by a factor of 2. Therefore, the neutral precursor was $\text{UCl}_5\text{AlCl}_3$. A very weak parent ion signal $\text{UCl}_5\text{AlCl}_3^+$ was also observed here.

The molecule $\text{UCl}_5\text{AlCl}_3$ observed in this phase of the work is in agreement with Gruen and McBeth, who also found that $\text{UCl}_5\text{AlCl}_3$ was the important new species in the presence of Cl_2 and AlCl_3 .

Comparison with Gruen and McBeth Results

Gruen and McBeth² have given free energy equations for the equilibria between solid UCl_4 and the various gaseous uranium-containing species. We can combine them with literature data to evaluate the equilibrium constants for the vapor equilibria that we studied and compare the results.

Table 5

RESULTS WITH $\text{UCl}_4 + \text{Cl}_2 + \text{AlCl}_3$

Ion	Electron Energy eV	a	b	c	d	Parent Molecule	Log ₁₀ Pressures (atm) Calculated for Each of Four Conditions			
Cl_2^+	14	120	94	10	60	Cl_2	-4.19	-4.30	- 5.26	-4.34
AlCl_2^+	20	540	1950	2000	2020	AlCl_3	-4.60	-4.21	- 4.20	-4.19
UCl_4^+	12.5	0.35	0.24	0.11	0.2	UCl_4	-6.40	-6.70	- 7.06	-6.8
UCl_5^+	20	1.0	0.69	0.09	0.6	UCl_5	-7.35	-7.66	- 8.55	-7.72
$\text{UCl}_3\text{AlCl}_3^+$	50	0.08	0.21	0.06	0.15	$\text{UCl}_4\text{AlCl}_3$	-9.85	-9.59	-10.13	-9.74
$\text{UCl}_4\text{AlCl}_3^+$	50	0.06	0.12	0.025	0.10	$\text{UCl}_5\text{AlCl}_3$	-9.80	-9.66	-10.34	-9.72

Temperature = 692°K

Equilibria		Log of Equilibrium Quotients			
(1)	$\text{UCl}_4 + \frac{1}{2} \text{Cl}_2 = \text{UCl}_5$	1.15	1.20	1.15	1.26
(2)	$\text{UCl}_4 + \text{AlCl}_3 = \text{UCl}_4\text{AlCl}_3$	1.15	1.34	1.11	1.23
(3)	$\text{UCl}_4 + \frac{1}{2} \text{Cl}_2 + \text{AlCl}_3 = \text{UCl}_5\text{AlCl}_3$	3.30	3.340	3.53	3.41
(4)	$2 \text{UCl}_4 + \text{AlCl}_3 = \text{U}_2\text{Cl}_8\text{AlCl}_3$	7.54	8.04	8.18	8.00
(5)	$\text{UCl}_4 + 2 \text{AlCl}_3 = \text{UCl}_4\text{Al}_2\text{Cl}_6$	5.75	5.53	5.32	5.41
(6)	$2 \text{UCl}_4 + \text{Cl}_2 + \text{AlCl}_3 = \text{U}_2\text{Cl}_{10}\text{AlCl}_3$	9.50	9.53	10.96	9.90
(7)	$\text{UCl}_4 + \frac{1}{2} \text{Cl}_2 + 2 \text{AlCl}_3 = \text{UCl}_5\text{Al}_2\text{Cl}_6$	7.08	6.78	6.91	6.79

Footnote: The log $P(\text{UCl}_4\text{AlCl}_3)$ and log (equil. quotients) involving it should have an additive constant, q' , to take account of fragmentation. The log $P(\text{UCl}_5\text{AlCl}_3)$ and related equilibrium quotients should have an additive constant q'' . (Comparison with Reference ² indicates that q'' should be 1.54, see below).

The computations are given in Table 6. For U_2Cl_{10} (gas) the results are shown as Case A, for which $\log K$ is found to be 7.94 from the data of Reference 2 and from our data, $\log K$ equals $q + 6.06$. Therefore, from this comparison the quantity $q \simeq 1.9$ or the $U_2Cl_8^+$ ion intensity should be multiplied by 80 to give U_2Cl_{10} pressures in accord with Reference 2. Our equilibrium data indicate that the partial pressure of UCl_5 under the conditions of Gruen and McBeth's experiments would be several orders of magnitude lower than the U_2Cl_{10} pressure. Thus, UCl_5 could not have been of importance in their work.

For UCl_5AlCl_3 , Case B in Table 6, the $\log K$ values are 5.06 from Reference 2 and equal to $q' + 3.5$ from our results. Thus, q' is about 1.54 and the $UCl_4AlCl_3^+$ ion intensity should be multiplied by about 35 to give UCl_5AlCl_3 pressures in agreement with Reference 2.

For $UCl_4Al_2Cl_6$ the comparison made in Table 6 shows that the pressure of that molecule would have been too small in our experiment to be detectable, especially since it would be expected to fragment more than the other U-Al-Cl molecules.

Enhancement of UCl_4 Volatility by Cl_2 and $AlCl_3$

The pressures of some of the complex vapor species (UCl_4 , U_2Cl_{10} , $UCl_4Al_2Cl_6$, and UCl_5AlCl_3) can be calculated as a function of temperature and pressures of Cl_2 and $AlCl_3$ with literature information. The pressure of UCl_5 and UCl_4AlCl_3 can be evaluated as a function of pressure of Cl_2 and $AlCl_3$ from the present data at only one temperature ($\sim 700^\circ K$) because it was not possible to obtain reliable temperature coefficients in the time allotted for this study.

Table 6

COMPARISON OF EQUILIBRIUM CONSTANTS OF GREEN AND MCNETH WITH PRESENT DATA

<u>Equilibrium</u>	<u>Free Energy Equation</u>	<u>Ref.</u>
Case A: $2 \text{ UCl}_4(\text{s}) + \text{Cl}_2(\text{g}) = \text{U}_2\text{Cl}_{10}(\text{g})$	$15132 - 15.38 \text{ T}$	2
$\text{UCl}_4(\text{s}) = \text{UCl}_4(\text{g})$	$47700 - 47.7 \text{ T}$	5
<hr/>	<hr/>	
$2 \text{ UCl}_4(\text{g}) + \text{Cl}_2(\text{g}) = \text{U}_2\text{Cl}_{10}(\text{g})$	$-80268 + 80 \text{ T}$	
$\log K (690 \text{ K}) = 7.94$ (Green and McNeth)		
$\log K (960 \text{ K}) = 9 + 6.06$ (from our data)		
Case B: $\text{UCl}_5(\text{s}) + 1/2 \text{ Al}_2\text{Cl}_6(\text{g}) + 1/2 \text{ Cl}_2(\text{g}) = \text{UCl}_5\text{AlCl}_3(\text{g})$	$8914 - 15.74 \text{ T}$	2
$\text{UCl}_4(\text{s}) = \text{UCl}_4(\text{g})$	$47700 - 47.7 \text{ T}$	5
<hr/>	<hr/>	
$1/2 \text{ Al}_2\text{Cl}_6(\text{g}) = \text{AlCl}_3(\text{g})$	$14370 - 16.7 \text{ T}$	6
<hr/>	<hr/>	
$\text{UCl}_4(\text{g}) + \text{AlCl}_3(\text{g}) + 1/2 \text{ Cl}_2(\text{g}) = \text{UCl}_5\text{AlCl}_3(\text{g})$	$-53150 + 53.68 \text{ T}$	
$\log K (692^\circ\text{K}) = 5.06$ (Green + McNeth)		
$\log K (692^\circ\text{K}) = 9 + 3.5$ (from our data)		
Case C: $\text{UCl}_4(\text{s}) + \text{Al}_2\text{Cl}_6(\text{g}) = \text{UCl}_4\text{Al}_2\text{Cl}_6(\text{g})$	$15780 - 15.30 \text{ T}$	2
$\text{UCl}_4(\text{s}) = \text{UCl}_4(\text{g})$	$47700 - 47.7 \text{ T}$	5
<hr/>	<hr/>	
$1/2 \text{ Al}_2\text{Cl}_6(\text{g}) = \text{AlCl}_3(\text{g})$	$14370 - 16.70 \text{ T}$	6
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$\text{UCl}_4(\text{g}) + 2 \text{ AlCl}_3(\text{g}) = \text{UCl}_4\text{Al}_2\text{Cl}_6(\text{g})$	$-60660 + 65.8 \text{ T}$	
$\log K (690^\circ\text{K}) = 4.83$		
11 $\log P(\text{UCl}_4) = -5.5$		
$\log P(\text{AlCl}_3) = 4.9$		
then $\log P(\text{UCl}_4\text{Al}_2\text{Cl}_6) = -10.5$		

The total pressures of uranium chloride species in equilibrium with solid UCl_4 can be represented by:

$$P(\text{U, total}) = P(\text{UCl}_4) + P(\text{UCl}_5) + 2 P(\text{U}_2\text{Cl}_{10}) + P(\text{UCl}_4\text{AlCl}_3) + P(\text{UCl}_4\text{Al}_2\text{Cl}_6) + P(\text{UCl}_5\text{AlCl}_3).$$

The partial pressures of all the species can be calculated at 690°K as a function of pressure of Cl_2 and AlCl_3 from the expressions given in Table 7. For some species there is sufficient information to give the temperature coefficient, which is also shown in the table.

Table 7

EXPRESSIONS FOR PARTIAL PRESSURES (atm) OF
SPECIES AS A FUNCTION OF Cl_2 AND AlCl_3
PRESSURES (atm)

	Reference
$P(\text{UCl}_4) = \text{Antilog} \left(10.43 - \frac{10400}{T} \right)$	5
$P(\text{UCl}_4, 690^\circ\text{K}) = 2.3 \times 10^{-5}$	
$P(\text{UCl}_5, 690^\circ\text{K}) = 3.2 \cdot 10^{-4} P^{\frac{1}{2}}(\text{Cl}_2)$	
$P(\text{U}_2\text{Cl}_{10}) = p(\text{Cl}_2) \text{Antilog} \left(3.36 - \frac{3308}{T} \right)$	2
$P(\text{U}_2\text{Cl}_{10}, 690^\circ\text{K}) = 3.7 \cdot 10^{-2} P(\text{Cl}_2)$	
$P(\text{UCl}_4\text{AlCl}_3, 690^\circ\text{K}) = 3.7 \cdot 10^{-4} P(\text{AlCl}_3)$	
$P(\text{UCl}_4\text{Al}_2\text{Cl}_6) = P^2(\text{AlCl}_3) \text{Antilog} \left(\frac{2833}{T} - 3.96 \right)$	2, 6
$P(\text{UCl}_4\text{Al}_2\text{Cl}_6, 690^\circ\text{K}) = 1.4 P^2(\text{AlCl}_3)$	
$P(\text{UCl}_5\text{AlCl}_3) = P^{\frac{1}{2}}(\text{Cl}_2) P(\text{AlCl}_3) \text{antilog} \left(\frac{1193}{T} - 1.30 \right)$	2, 6
$P(\text{UCl}_5\text{AlCl}_3, 690^\circ\text{K}) = 2.7 P^{\frac{1}{2}}(\text{Cl}_2) P(\text{AlCl}_3)$	
$P(\text{Al}_2\text{Cl}_6) = P^2(\text{AlCl}_3) \text{Antilog} \left(-7.30 - \frac{6280}{T} \right)$	6
$P(\text{Al}_2\text{Cl}_6, 690^\circ\text{K}) = 63 P^2(\text{AlCl}_3)$	

RECOMMENDATIONS FOR FUTURE STUDY

The U-Al-Cl System

The results of this work have pointed up several areas requiring further study, if the thermochemistry and general chemical behavior of the U-Al-Cl system are to be clarified.

(1) Fragmentation Patterns

As noted earlier, lack of information about electron impact fragmentation of the large dimer molecules precludes a reliable thermodynamic treatment. This information could be obtained from a careful study of intensity ratios of the pertinent species under a wide variety of conditions. A more detailed study of the ionization efficiency behavior would also be useful in this regard.

(2) Temperature Dependence of U-Al-Cl Equilibria

Any further extension of the present work requires a careful second-law study of the various equilibria. Now that the general features of the U-Al-Cl chemistry are established, accurate temperature studies can be made and additional thermodynamic data derived.

(3) Vapor Pressure of UCl_4

This information is central to the interpretation of all the data presented here. However, the literature data on the subject are both sketchy and discordant. It would be valuable to have an accurate determination on a high purity sample in the 10^{-4} to 10^{-2} torr range. This could be done readily by the torsion-effusion method, which we are currently using for other studies in our laboratory.

Gaseous Uranium-Halides

For uranium isotope separation by laser excitation, it is important to obtain a better understanding of the chemistry of the lower valent uranium halides, especially the fluorides. That is, the volatility of the halides is much greater than that of uranium itself; therefore, reasonable vapor concentrations of uranium halides can be obtained at temperatures well below those required with pure uranium. However, there is almost nothing about the stabilities of the lower valent gaseous uranium halides. For laser isotope separation purposes, the molecule UF would probably be the most interesting because natural F is isotopically pure and because the U-F bond is stronger than the bond with other halides. The stability of that molecule relative to all the other gaseous U-F species (U, UF₂, UF₃, UF₄, UF₅, UF₆) needs to be determined to know the conditions under which it can be generated in a relatively pure state. Except for UF₆ and UF₄, no information on the stabilities of those species is available.

Similar investigations on the other halides (Cl, Br, I) can serve to indicate conditions under which they may be useful for laser isotope separation (LIS).

Much of the information required can be obtained by mass spectrometric techniques, which also yield accurate ionization potentials of interest to LIS.

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