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Vapor Complexes of Uranium Pentachloride and Uranium Tetrachloride with Aluminum Chloride. The Nature of Gaseous Uranium Pentachloride

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The following three reactions were studied spectrophotometrically: (1) $2UCl_4(s) + Cl_2(g) = U_2Cl_{10}(g)$, $\Delta F = 15{,}132 - 15.38T$ cal/mol (450–650°K); (2) $UCl_4(s) + {}^1/_2Al_2Cl_6(g) + {}^1/_2Cl_2(g) = UCl_5 \cdot AlCl_3(g)$, $\Delta F = 8914 - 10.74T$ cal/mol (440–630°K); (3) $UCl_4(s) + Al_2Cl_6(g) = UCl_2(AlCl_4)_2(g)$, $\Delta F = 15{,}780 - 15.30T$ cal/mol (600–800°K). The volatility ratios $V_T = (P_{UCl_2(AlCl_4)_2}$ in 1 atm of $Al_2Cl_6)/P_{UCl_4}$ are found to be $\sim 10^7$ at 500°K, $\sim 10^4$ at 600°K, and $\sim 10^3$ at 700°K. The partial pressure of $UCl_5 \cdot AlCl_3$ is 34 mm at 500°K, 1 atm of Al_2Cl_6, and 1 atm of Cl_2. Uranium pentachloride was found to vaporize as a dimer molecule. The electronic absorption spectrum of gaseous U_2Cl_{10} was interpreted in terms of two Cl octahedra sharing an edge with U atoms at positions of approximately octahedral symmetry.

Introduction

Recognition of the existence of volatile complexes between aluminum chloride and metal chlorides widely distributed throughout the periodic table has motivated recent work on the neodymium chloride–aluminum chloride complex.[1,2] It is of interest to extend such studies to a variety of different metal halide systems in order to discover the stoichiometries and molecular structures of the vapor species, to gain an insight into the factors governing the stabilities and relative volatilities of the complexes, and to determine the thermodynamics of the reactions.

The existence and some properties of the uranium tetrachloride–aluminum chloride complex have been described.[3] The present paper gives additional data and a more complete analysis of this system, as well as of the uranium pentachloride–aluminum chloride system. An important prerequisite for an understanding of the latter system is information concerning gaseous uranium pentachloride. The first part of the paper, therefore, is devoted to an account of an investigation of the nature of gaseous uranium pentachloride.

Results and Discussion

Uranium Pentachloride.—Uranium pentachloride was discovered by Roscoe[4] in 1874 as a by-product of the preparation of UCl_4. The compound is thermally unstable decomposing[5] in an inert atmosphere below 525°K to UCl_4 and Cl_2 or disproportionating to UCl_4 and UCl_6 between 370 and 450°K under a high vacuum.[6] Because of this behavior, doubts have been expressed concerning the possibility of UCl_5 existing as a vapor above 330°K where its vapor pressure is estimated to be $\sim 10^{-7}$ mm.[6]

Gaseous uranium pentachloride is readily formed in a sealed cell containing UCl_4 and Cl_2 gas as described in the Experimental Section. The spectra of UCl_5 between 597 and 1031°K are reproduced in Figure 1. The molar absorptivities of the vapor species were determined in separate experiments in which cells containing 10 mg of UCl_4 and 2 atm of Cl_2 were employed. The absorbance of the 6658-cm^{-1} peak was followed as a function of temperature and found to remain nearly constant between 575 and 625°K showing that all of the UCl_4 initially added to the cell had vaporized. The measured absorbance from 4000 to 12,000 cm^{-1} is due solely to UCl_5 since Cl_2 does not absorb in this spectral region. Furthermore, UCl_4 does not contribute to the absorption at temperatures less than 675°K since its vapor pressure is 10^{-2} mm.

The relation

$$\epsilon = A/cl \tag{1}$$

where ϵ is the molar absorptivity, A is the absorbance, c is the concentration in moles per liter, and l is the path length in centimeters was used to calculate the molar absorptivities employing the measured absorbances, the known cell volume, the cell path length, and the amount of UCl_4 weighed into the cell. The ϵ's are readily obtainable from the curves shown in Figure 1; $\epsilon_{6658\ cm^{-1}}$ is 19.

It is obvious from an examination of Figure 1 that the UCl_5 spectrum undergoes drastic changes with temperature. The most obvious changes involve a decrease in the intensity of the 6658-cm^{-1} peak with increasing temperature and the simultaneous appearance of prominent absorption bands at 7215 and 8197 cm^{-1}. The "low" temperature spectrum (curve A in Figure 1 and curve B in Figure 2) persists virtually unchanged in the temperature range 450–650°K, strongly indicating that a single vapor species is responsible for the light absorption.

In order to identify the "low" temperature vapor species, which has up to now been assumed to be UCl_5, a series of experiments at different Cl_2 pressures was performed. Measured amounts of Cl_2 gas were condensed into cells containing 0.1–0.2 g of UCl_4 so as to give 0.88 atm (expt 39E), 1.8 atm (expt 35E), and 3.4 atm (expt 42E) of pressure at 298°K. Spectra were

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[1] D. M. Gruen and H. A. Øye, *Inorg. Nucl. Chem. Letters*, **3**, 453 (1967).

[2] H. A. Øye and D. M. Gruen, *J. Am. Chem. Soc.*, **91**, 2229 (1969).

[3] D. M. Gruen and R. L. McBeth, *Inorg. Nucl. Chem. Letters*, **4**, 299 (1968).

[4] H. Roscoe, *Ber.*, **7**, 1131 (1874).

[5] H. Martin and K. H. Eldau, *Z. Anorg. Allgem. Chem.*, **251**, 295 (1943).

[6] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," NNES, VIII-5, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp 496, 497.

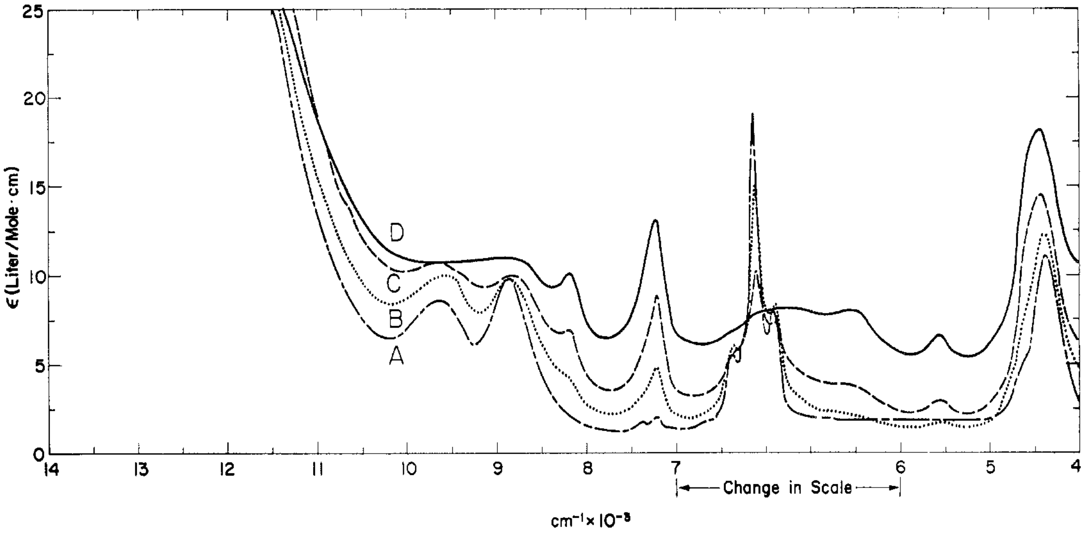

Figure 1.—Absorption spectra of gaseous uranium pentachloride at various temperatures: A, 597°K; B, 747°K; C, 844°K; D, 1031°K.

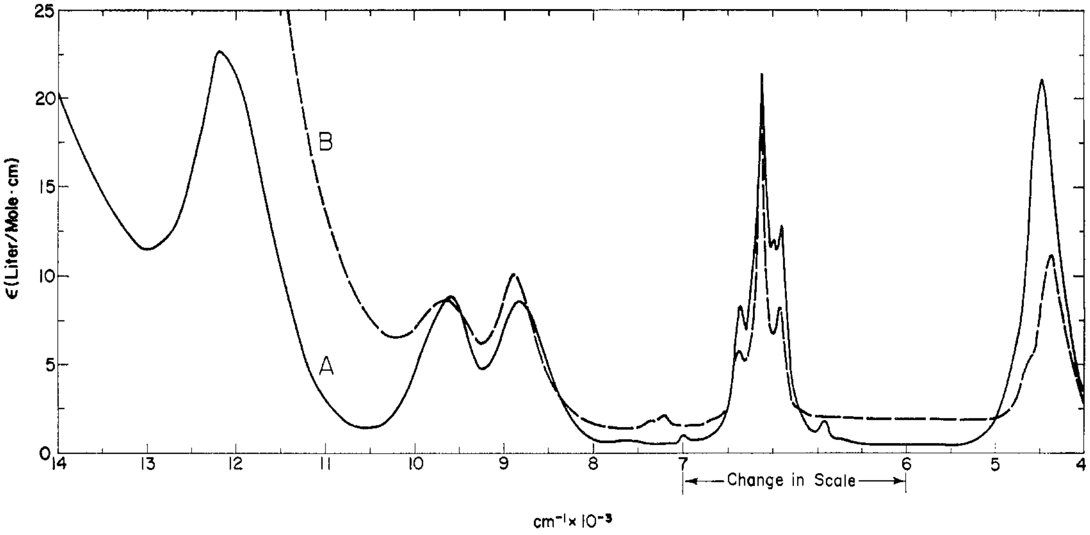

Figure 2.—Absorption spectra of gaseous $UCl_5 \cdot AlCl_3$ complex at 596°K (A) and of gaseous U_2Cl_{10} at 597°K (B).

measured in the range 450–650°K. The vapor pressure of the gaseous uranium species was determined from the measured absorbancies and the previously determined ε's using the relation

$$P_{atm} = ART/\epsilon l \qquad (2)$$

The data obtained in this series of experiments are listed in Table I with pressures in millimeters calculated for the U_2Cl_{10} dimer. The data were evaluated by considering the three equilibria

$$2UCl_4(s) + Cl_2(g) = U_2Cl_{10}(g) \qquad (3)$$

$$UCl_4(s) + {}^1/_2Cl_2(g) = UCl_5(g) \qquad (4)$$

$$2UCl_4(s) + 2Cl_2(g) = UCl_5Cl_2UCl_5(g) \qquad (5)$$

The Cl_2 pressures listed in Table I have been corrected for Cl_2 consumption due to reaction 3.

Calculations were made of log K for each of the three reactions using all of the data points listed in Table I. The results of the calculations are shown graphically in Figure 3 where the log K's are plotted *vs.* $1/T_{min}$ with least-squares lines drawn through the points. The sums of the squared deviations are 0.018, 0.200, and 0.903 for equilibria 3, 4, and 5, respectively. Equilibrium 3 thus forms the basis of a significantly better fit for the data in the 450–650°K range than either (4) or (5). A consideration of these findings leads to the conclusion that the reaction of Cl_2 with UCl_4 results in the formation of U_2Cl_{10} dimer molecules.

The free energy change for reaction 3 in the range 450–650°K is calculated to be

$$\Delta F = -RT \ln K = 15{,}132 - 15.38T \text{ cal/mol} \qquad (6)$$

It is to be noted that K for reaction 3 is a dimensionless quantity. The pressure of U_2Cl_{10} dimer as a function of temperature and Cl_2 pressure is given by

$$\log P_{U_2Cl_{10}} = -\frac{3307}{T} + 3.361 + \log P_{Cl_2} \qquad (7)$$

The existence of U_2Cl_{10} dimer molecules in the vapor phase is of considerable interest. The crystal structure of UCl_5 has recently been found by Smith, *et al.*,[7] to be

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[7] G. S. Smith, Q. Johnson, and R. E. Elson, *Acta Cryst.*, **22**, 300 (1967).

TABLE I

DATA FOR THE REACTION

$n_1UCl_4(s) + n_2Cl_2(g) = U_{n_1}Cl_{4n_1+2n_2}$

Conditions	T_{min}, °K	$\overline{T}$, °K	Pressure, mm			Absorbance
			$P^0_{Cl_2}$	P_{Cl_2}	$P_{U_2Cl_{10}}$	
Expt 35E	545.4	554	2541	2536	4.86	0.110
W_{UCl_4} = 0.0760 g	571.6	578	2651	2641	9.83	0.213
$P^0_{Cl_2}$ at 298°K = 1367 mm	597.2	602	2762	2744	18.26	0.380
V = 59.84 ml	610.2	616	2826	2798	28.03	0.570
l = 20.54 cm	648.4	655	3005	2945	59.62	1.140
Expt 39E	574.2	581	1304	1299	4.93	0.104
W_{UCl_4} = 0.0360 g	587.0	593	1331	1324	7.26	0.150
$P^0_{Cl_2}$ at 298°K = 669 mm	627.0	633	1421	1403	17.83	0.345
V = 60.49 ml						
l = 20.09 cm						
Expt 42E	541.0	549	4808	4798	9.52	0.204
W_{UCl_4} = 0.1538 g	567.7	574	5027	5011	15.95	0.327
$P^0_{Cl_2}$ at 298°K = 2610 mm	529.8	537	4703	4697	6.34	0.139
V = 73.5 ml	554.1	561	4913	4901	11.68	0.245
l = 19.30 cm	580.4	586	5132	5110	21.91	0.440
	608.0	615	5386	5344	42.33	0.810
	634.8	641	5614	5537	77.34	1.420
	660.8	667	5842	5719	122.99	2.170
	594.4	600	5255	5223	32.12	0.630
	460.7	472	4134	4133	0.68	0.017
	512.8	522	4572	4569	3.37	0.076
	482.8	494	4327	4326	1.47	0.035
	498.8	509	4458	4456	2.21	0.051

based on cubic closest packing of chlorine atoms, in which uranium atoms occupy one-fifth of the octahedral holes. Two such octahedra share an edge to form a U_2Cl_{10} dimeric unit. U–Cl distances involving bridging Cl are 2.67 and 2.70 Å; those involving nonbridging Cl are 2.43, 2.43, 2.44, and 2.44 Å. Uranium atoms in the U_2Cl_{10} units are each shifted by about 0.20 Å from the centers of the octahedra away from each other. In the solid, therefore, the dimeric form is a well-established entity. However, the only previous information concerning the independent existence of U_2Cl_{10} is an ebullioscopic study of a solution of UCl_5 in CCl_4 which found the molecular weight of the dissolved species to correspond quite closely to that of the dimer.[8]

The dimeric configuration of U_2Cl_{10} in the solid is very similar to that found in crystalline $NbCl_5$ and $TaCl_5$,[9] in $MoCl_5$,[10] in $ReCl_5$,[11] and in $PaBr_5$[12] but differs completely from the infinite chains of pentagonal bipyramids sharing edges found in $PaCl_5$.[13] Of these compounds, $NbCl_5$ appears to have been studied most intensively in solution and in the vapor phase.[14] The occurrence of Nb_2Cl_{10} dimers has been demonstrated by ebullioscopic[15] and by spectroscopic studies[14] of solutions of $NbCl_5$ in CCl_4. However, gaseous $NbCl_5$ has been shown by vapor density measurements[16] and by ir spectra of matrix-isolated molecules[14] to be monomeric. The U_2Cl_{10} molecule, therefore, appears to be the first dimer to be identified in the gas phase for this series of metal pentachlorides.

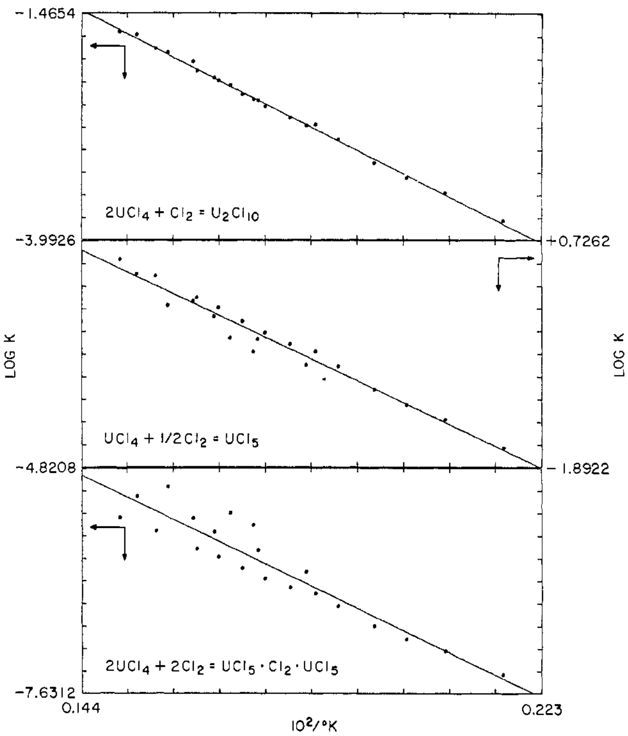

Figure 3.—Plots of log K vs. $1/T_{min}$ for reactions 3–5.

The electronic spectrum of the gaseous U_2Cl_{10} dimer molecule (Figure 2B) is remarkably similar to the spectra of a number of salts of the type R_4NUCl_6 ($R = CH_3$, n-C_3H_7) or $MUCl_6$ (M = Rb, Cs) dissolved in a variety of nonaqueous solvents such as $SOCl_2$, $POCl_3$, CH_3CN, and CH_3NO_2.[17] Selbin, Ortego, and Gritzner interpreted these solution spectra[17] on the reasonable assumption that they were due to the octahedral complex ion UCl_6^-. The similarity of the U_2Cl_{10} and the UCl_6^- spectra shows that the uranium atoms in the U_2Cl_{10} dimer molecules are also in positions of approximately octahedral symmetry. The close correspondences of the energies of the absorption maxima furthermore indicates that the ligand field splitting experienced by the single unpaired 5f electron due to six nearest chloride neighbors is comparable in U_2Cl_{10} and in UCl_6^-.

Under the combined influence of the spin–orbit coupling interaction and a ligand field of octahedral symmetry, the ^2F state splits up into five energy levels[18–22] whose labels in terms of the irreducible representations of the double group are shown in Figure 4.

The absorption bands of U_2Cl_{10} may be assigned as follows. The lowest energy band with maximum at 4386 cm^{-1} is assigned to the transition $\Gamma_7 \rightarrow \Gamma_8$. The

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(8) H. L. Gorin, R. S. Lowrie, and J. V. Hubbard, Report CD-5.350.8, Feb 28, 1946; quoted in ref 6, p 493, as CEW-TEC 29.

(9) A. Zalkin and D. E. Sands, *Acta Cryst.*, **11**, 615 (1958).

(10) D. E. Sands and A. Zalkin, *ibid.*, **12**, 723 (1959).

(11) K. Mucker, G. S. Smith, and Q. Johnson, *ibid.*, **B24**, 874 (1968).

(12) D. Brown, T. J. Petcher, and A. J. Smith, *Nature*, **217**, 737 (1968).

(13) R. P. Dodge, G. S. Smith, Q. Johnson, and R. E. Elson, *Acta Cryst.*, **22**, 85 (1967).

(14) R. D. Werder, R. A. Frey, and Hs. H. Gunthard, *J. Chem. Phys.*, **47**, 4159 (1967). References to the earlier literature on $NbCl_5$ can be found in this paper.

(15) D. Kepert and R. Nyholm, *J. Chem. Soc.*, 2871 (1965).

(16) L. Nisel'son, A. Pustil'nik, and T. Sokolova, *Russ. J. Inorg. Chem.*, **9**, 574 (1964).

(17) J. Selbin, J. D. Ortego, and G. Gritzner, *Inorg. Chem.*, **7**, 976 (1968); J. Selbin and J. D. Ortego, *Chem. Rev.*, **69**, 657 (1969).

(18) G. L. Goodman and M. Fred, *J. Chem. Phys.*, **30**, 849 (1959).

(19) J. D. Axe, H. J. Stapleton, and C. D. Jeffries, *Phys. Rev.*, **121**, Series 2, 1630 (1961).

(20) J. C. Eisenstein and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A255**, 181 (1960).

(21) D. G. Karraker, *Inorg. Chem.*, **3**, 1618 (1964).

(22) M. J. Reisfeld and G. A. Crosby, *ibid.*, **4**, 65 (1965).

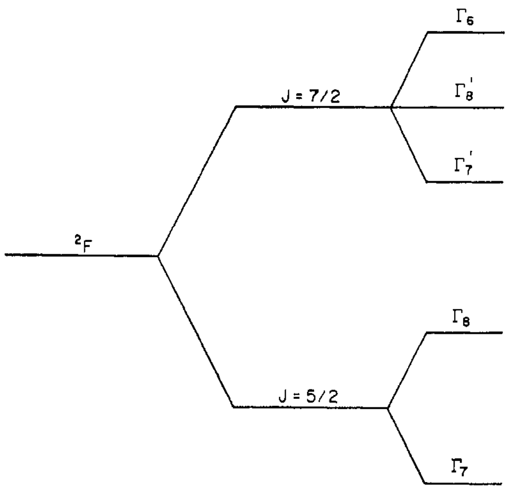

Figure 4.—Schematic energy level diagram for a ^{2}F state split by the combined action of the spin–orbit coupling and octahedral ligand field perturbations.

next group of bands whose most intense component is at 6658 cm^{-1} is assigned to the $\Gamma_7 \rightarrow \Gamma_7'$ transition. The structure within this band is presumably vibronic in origin. Satten and coworkers[23,24] had shown that the absorption spectrum of the UCl_6^{2-} complex ($5f^2$ configuration) may be understood on the basis of vibronic coupling involving electronic dipole transitions arising from simultaneous change in electronic state and a quantum of an odd vibrational mode of the UCl_6^{2-} complex. For octahedral symmetry, the $0 \rightarrow 0$ transitions are very strongly forbidden and the observed spectrum arises from a vibronic interaction of the $0 \rightarrow 0$ transition with one quantum of an odd mode of the molecule. Since there is no information on the vibrational spectrum of the dimer molecule, it is premature to attempt an analysis of the vibronic structure of the band in the 6600-cm^{-1} region. However, we call attention to a weak absorption band at 6369 cm^{-1} in the $UCl_5 \cdot AlCl_3$ complex spectrum (Figure 2A) and tentatively assign this band to the $\Gamma_7 \rightarrow \Gamma_7'$ $(0 \rightarrow 0)$ transition.

The next pair of absorption bands located at 8850 and 9615 cm^{-1} is assigned to the $\Gamma_7 \rightarrow \Gamma_8'$ transition which, as pointed out by Eisenstein and Pryce,[20] could experience a Jahn–Teller splitting of considerable magnitude. The 765-cm^{-1} splitting of the Γ_8' level found for U_2Cl_{10} is somewhat larger than that for UCl_6^- (540 cm^{-1}) but smaller than the value 825 cm^{-1} found for a solution of the uranium pentachloride–trichloroacrylyl chloride addition compound in $SOCl_2$[17] in which a species with C_{4v} symmetry presumably gives rise to the spectrum.

An intense charge-transfer band obscures the highest energy $\Gamma_7 \rightarrow \Gamma_6$ transition in the case of U_2Cl_{10}. However, the charge-transfer band is shifted to higher energies in the case of the aluminum chloride complex (Figure 2A) thus revealing the $\Gamma_7 \rightarrow \Gamma_6$ transition at 12,195 cm^{-1}. The close similarity of the U_2Cl_{10} and the aluminum chloride–uranium pentachloride vapor spectra in the 4000–10,000-cm^{-1} region leads one to suspect that the $\Gamma_7 \rightarrow \Gamma_6$ transition occurs at about the same energy in both molecules.

It is tempting to speculate as to the nature of the process responsible for the temperature variation in the U_2Cl_{10} spectrum (Figure 1). There appears to be a correlation, which has not yet been quantitatively evaluated, between the decreasing intensity of the 6658-cm^{-1} band and the increase in the intensity of the 7215-cm^{-1} band. Whether these spectral changes can be interpreted on the basis of a dissociative equilibrium of the type

$$U_2Cl_{10}(g) = 2UCl_5(g) \qquad (8)$$

is a problem requiring further investigation.

Uranium Pentachloride–Aluminum Chloride Vapor Complex.—Having established that in the temperature range 450–650°K the reaction of $Cl_2(g)$ with $UCl_4(s)$ results in the formation of U_2Cl_{10} dimer molecules in which the uranium atoms are in a distorted octahedral environment, it was of interest to determine if uranium pentachloride forms a vapor complex with aluminum chloride, to study the thermodynamics of such a reaction, and to establish the stoichiometry and molecular geometry of the complex species.

The equilibrium

$$n_1UCl_4(s) + n_2Al_2Cl_6(g) + n_3Cl_2(g) = U_{n_1}Al_{2n_2}Cl_{4n_1+6n_2+2n_3}(g) \qquad (9)$$

was studied spectrophotometrically. Sealed quartz optical cells were used containing known amounts of $UCl_4(s)$, $AlCl_3(s)$, and $Cl_2(g)$. The amounts of $AlCl_3$ were adjusted so that all of the $AlCl_3$ in the cell was in the vapor phase at 440°K and above. In the temperature range of the measurements, 440–630°K, the vapor pressure of pure UCl_4 is very low and $UCl_4(g)$ does not contribute to the absorption of light. The measured optical densities in the visible region are therefore due only to the UCl_5-containing species. Three types of experiments were carried out.

(a) It was ascertained by visual inspection and by X-ray analysis that the solid phase present in equilibrium with $Al_2Cl_6(g)$ and $Cl_2(g)$ at 400°K and above was UCl_4.

(b) The molar absorptivity of the complex was determined in a manner identical with that described for gaseous U_2Cl_{10} except that the experiment was performed in the presence of 2 atm of $Al_2Cl_6(g)$ and $Cl_2(g)$. The molar absorptivities of the U(V)–Al–Cl complex at selected wavelengths of absorption at 596°K are listed in Table II. No consistent variation

Table II

Molar Absorptivities (ϵ) of the $UCl_5 \cdot AlCl_3$ Complex at 596°K

Cm^{-1}	ϵ	Cm^{-1}	ϵ	Cm^{-1}	ϵ
4484	21.0	6649	21.3	7,604	0.6
6297	0.8	6748	8.2	8,850	8.5
6369	1.8	7003	1.0	9,615	8.8
6562	12.8	7194	0.5	12,195	22.7
6605	11.9				

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[23] R. A. Satten, D. J. Young, and D. M. Gruen *J. Chem. Phys.*, **33**, 1140 (1960).

[24] S. A. Pollack and R. A. Satten, *ibid.*, **36**, 804 (1962).

TABLE III

DATA FOR THE REACTION

$n_1UCl_4(s) + n_2Al_2Cl_6(g) + n_3Cl_2(g) = U_{n_1}Al_{2n_2}Cl_{4n_1+6n_2+2n_3}(g)$

			Pressure at $\bar{T}$, mm						
Conditions	T_{min}, °K	$\bar{T}$, °K	$P^0_{Al_2Cl_6}$	$P'_{Al_2Cl_6}$	$P_{Al_2Cl_6}$	$P^0_{Cl_2}$	P_{Cl_2}	$P_{U(V)-Al-Cl}$ complex	Absorbance
Expt 30E	456.3	467	1004	1004	999	596	591	9.67	0.146
$W_{UCl_4} = 0.1165$ g	462.4	473	1017	1017	1011	603	597	11.07	0.165
$W_{Al_2Cl_6} = 0.5774$ g	464.6	476	1023	1023	1017	607	601	11.88	0.176
$P^0_{Cl_2}$ at 298°K = 380 mm	486.2	497	1069	1068	1058	634	625	18.33	0.260
$V = 62.75$ ml	515.3	524	1127	1125	1109	668	652	31.96	0.430
$l = 20.63$ cm	542.7	551	1185	1181	1156	703	677	51.58	0.660
	569.6	576	1238	1232	1193	734	694	79.24	0.970
	571.9	578	1243	1236	1193	737	694	86.89	1.060
	596.3	602	1294	1284	1226	768	710	116.11	1.360
	622.7	629	1352	1334	1262	802	729	145.41	1.630
Expt 40E	429.6	441	1020	1020	1017	1305	1302	6.86	0.110
$W_{UCl_4} = 0.0174$ g	438.2	450	1041	1041	1039	1332	1328	8.97	0.141
$W_{Al_2Cl_6} = 0.5894$ g	445.2	456	1055	1055	1049	1350	1345	10.50	0.163
$P^0_{Cl_2}$ at 298°K = 882 mm	458.6	470	1087	1087	1079	1391	1383	15.41	0.232
$V = 59.53$ ml	475.5	486	1124	1124	1113	1438	1427	22.12	0.322
$l = 20.70$ cm									
Expt 41E	556.3	563	2452	2446	2403	778	734	87.16	1.027
$W_{UCl_4} = 0.1702$ g	583.2	589	2566	2554	2482	814	741	145.52	1.639
$W_{Al_2Cl_6} = 1.0364$ g	610.6	617	2687	2667	2573	853	760	186.94	2.010
$P^0_{Cl_2}$ at 298°K = 412 mm	490.2	501	2182	2181	2167	693	679	27.94	0.370
$V = 55.60$ ml	519.4	528	2300	2297	2273	730	705	49.34	0.620
$l = 19.41$ cm	543.4	551	2400	2395	2359	762	725	73.50	0.885
	570.0	576	2509	2500	2445	796	740	111.57	1.285
	596.7	602	2622	2607	2567	832	751	161.52	1.780
	623.3	629	2740	2727	2604	870	760	220.92	2.330
	517.1	526	2291	2289	2260	727	700	54.71	0.690
Expt 43E	510.2	520	2454	2452	2408	3062	3018	87.02	1.105
$W_{UCl_4} = 0.1405$ g	533.9	543	2562	2558	2493	3198	3131	133.22	1.620
$W_{Al_2Cl_6} = 0.995$ g	496.1	506	2388	2386	2358	2980	2951	57.24	0.747
$P^0_{Cl_2}$ at 298°K = 1755 mm	510.0	520	2454	2452	2404	3062	3015	92.92	1.180
$V = 49.27$ ml	523.4	532	2510	2507	2439	3133	3065	136.16	1.690
$l = 19.32$ cm	532.0	541	2553	2549	2469	3186	3118	158.94	1.940
	545.6	553	2610	2604	2519	3257	3171	172.94	2.065

of the ϵ's was found in the range 440–630°K, although appreciable spectral changes were noted at higher temperatures as discussed below.

(c) In order to determine n_1, n_2, and n_3 in eq 9, a series of experiments with excess $UCl_4(s)$ and varying $Al_2Cl_6(g)$ and Cl_2 pressures was performed. The data are listed in Table III. In the four experiments of this series, the $Al_2Cl_6(g)$ and $Cl_2(g)$ pressures at 500°K were, respectively, 2.9 and 0.9 atm (expt 41E); 3.1 and 3.9 atm (expt 43E); 1.5 and 1.9 atm (expt 40E); 1.4 and 0.8 atm (expt 30E).

In Table III, $P^0_{Al_2Cl_6}$ gives the pressure of $Al_2Cl_6(g)$ calculated from the ideal gas law at the average cell temperature, $\bar{T}$. The manner in which $\bar{T}$ was obtained is described in the Experimental Section. An approximate calculation of the Al_2Cl_6 pressure using the van der Waals equation of state showed the pressures to differ from the ideal gas law pressure by less than 1% and this correction was omitted. There are, however, two corrections to the $Al_2Cl_6(g)$ pressure which must be taken into account. The first is due to the dissociation reaction[25–27]

$$Al_2Cl_6(g) = 2AlCl_3(g) \qquad (10)$$

The equilibrium constant, K, for equilibrium 10 was calculated from values tabulated in JANAF tables[28] for $400°K \leq \bar{T} \leq 1000°K$. These values, when fitted to the function

$$\log K = A + (B/T) + (C/T^2) \qquad (11)$$

by the method of least squares, give

$$\log K = 6.649 - (5.684 \times 10^3/T) - (1.607 \times 10^5/T^2) \qquad (12)$$

The dimer pressure corrected for equilibrium 10 only is given by

$$P'_{Al_2Cl_6} = 0.5[2P^0_{Al_2Cl_6} + (K/4) - \sqrt{P^0_{Al_2Cl_6}K + (K^2/16)}] \qquad (13)$$

The second correction is due to the consumption of Al_2Cl_6 in reaction 9. In Table III, $P_{Al_2Cl_6}$ is the dimer pressure corrected for reaction 10 and for reaction 9 with $n_2 = {}^1/_2$. Chlorine pressures were calculated for $\bar{T}$ using the ideal gas law and have been corrected for Cl_2 consumption due to reaction 9 with $n_2 = {}^1/_2$. The partial pressures of the U(V)–Al–Cl complex listed in

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(25) W. Fischer, O. Rahlfs, and B. Benze, *Z. Anorg. Allgem. Chem.*, **205**, 1 (1932).

(26) A. Smits and J. L. Meijering, *Z. Physik. Chem.*, **B41**, 98 (1938).

(27) G. E. Vrieland and D. R. Stull, *J. Chem. Eng. Data*, **12**, 532 (1967).

(28) "JANAF Thermochemical Data," The Dow Chemical Co., Thermal Laboratory, Midland, Mich.

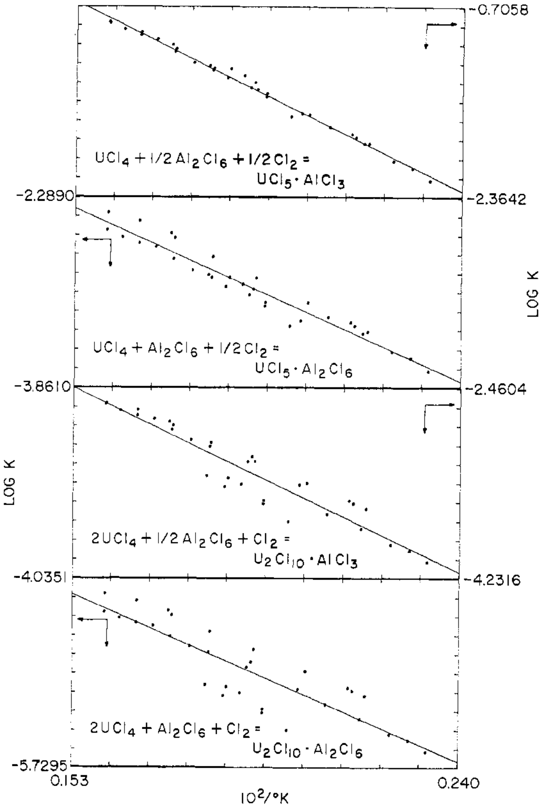

Figure 5.—Plots of log K *vs.* $1/T_{min}$ for eq 9 using four different sets of n_1, n_2, and n_3 values.

Table III were calculated for $\bar{T}$ using eq 2 with $\epsilon_{U(V)-Al-Cl} = 21.3$ l./mol cm at 6649 cm^{-1}. The listed pressures are for a mononuclear uranium vapor species.

There are a number of ways in which the data of Table III could be treated in order to extract values of n_1, n_2, and n_3. The approach adopted here was to chose reasonable values of n_1, n_2, and n_3 and to plot log K for reaction 9 as a function of $1/T_{min}$. The results are shown graphically in Figure 5 with least-squares lines drawn through the points. The sums of the squared deviations are 0.032, 0.20, 0.56, and 1.07 for the following sets of n_1, n_2, n_3 values: 1, 0.5, 0.5; 1, 1, 0.5; 2, 0.5, 1; 2, 1, 1, respectively. It is seen, therefore, that of the four sets of likely n_1, n_2, and n_3 values, the set with $n_1 = 1$, $n_2 = 0.5$, $n_3 = 0.5$ gives a significantly better fit to the data than the other three. Our data therefore can be consistently interpreted in terms of the equilibrium

$$UCl_4(s) + {}^1/_2Al_2Cl_6(g) + {}^1/_2Cl_2(g) = UCl_5 \cdot AlCl_3(g) \quad (14)$$

The free energy change for reaction 14 in the range 440–630°K is calculated to be

$$\Delta F = 8914 - 10.74T \text{ cal/mol} \quad (15)$$

It is to be noted that K for reaction 14 is a dimensionless quantity. The partial pressure of $UCl_5 \cdot AlCl_3(g)$ as a function of temperature and $Al_2Cl_6(g)$ and $Cl_2(g)$ pressures is given by

$$\log P_{UCl_5 \cdot AlCl_3} = -\frac{1948}{T} + 2.347 + {}^1/_2 \log P_{Al_2Cl_6(g)} + {}^1/_2 \log P_{Cl_2(g)} \quad (16)$$

A few words are in order regarding the reason for plotting log K *vs.* T_{min} rather than $\bar{T}$.

Solid UCl_4 originally in other parts of the cell is transported to the point of minimum temperature and equilibrium 14 is established there. The partial pressures of $UCl_5 \cdot AlCl_3$, Al_2Cl_6, and Cl_2, however, will be dependent on the average temperature distribution throughout the cell. A reasonable way to take this fact into account is to use an average temperature, $\bar{T}$, to calculate the pressures but to use the minimum cell temperature, T_{min}, for calculating the equilibrium constant of the reaction 14.

One can calculate the partial pressures of the $UCl_5 \cdot AlCl_3$ complex in the UCl_4–Al_2Cl_6–Cl_2 system and U_2Cl_{10} in the UCl_4–Cl_2 system as a function of temperature from eq 16 and 7, respectively. For $UCl_5 \cdot AlCl_3$, at 1 atm of Al_2Cl_6 and 1 atm of Cl_2 pressure, $P_{complex}$ turns out to be 34 mm at 500°K and 87 mm at 600°K. For U_2Cl_{10} at 1 atm of Cl_2 pressure, P_{dimer} is 0.44 mm at 500°K and 5.5 mm at 600°K. The ratio of partial pressures of uranium-containing vapor species on a per mole of uranium basis is 36 at 500°K and 8 at 600°K.

At 420°K, the vapor pressure of Al_2Cl_6 is 0.1 atm.[26] If a gas mixture consisting of 0.1 atm of Al_2Cl_6 and 0.9 atm of Cl_2 were to be passed over solid UCl_4 at 420°K (147°), the resultant gas stream would contain a partial pressure of $UCl_5 \cdot AlCl_5$ of 1.3 mm under equilibrium conditions. If in a similar experiment conducted in the absence of Al_2Cl_6, a stream of Cl_2 gas at 420°K and 1 atm pressure were passed over UCl_4, the saturated vapor would contain a partial pressure of 0.024 mm of U_2Cl_{10}. The addition of 0.1 atm of Al_2Cl_6 to the gas stream therefore is calculated to result in an increased volatility of uranium, on a per mole basis, by a factor of 27.

The remarkable similarity of the $UCl_5 \cdot AlCl_3$ spectrum (Figure 2A) and the "octahedral" U_2Cl_{10} spectrum (Figure 2B) can be accounted for on the assumption that the uranium atom in $UCl_5 \cdot AlCl_3$ is also situated at a site of octahedral symmetry. A plausible structure for the complex molecule therefore is one in which a [UCl_6] octahedron shares an edge with an [$AlCl_4$] tetrahedron. Both the energies and the molar absorptivities of the transitions are very closely similar for U_2Cl_{10} and $UCl_5 \cdot AlCl_3$, with the exception of the lowest energy band. An even more remarkable circumstance is the close correspondence of the vibronic fine structure in the 6000–7000-cm^{-1} region. It appears that the vibrational frequencies of the [UCl_6] octahedron which are coupled to electronic transitions of the 5f configuration are not seriously perturbed in going from the dimer to the aluminum chloride complex.

Using free energy eq 6 and 15, one calculates ΔF for the reaction

$$U_2Cl_{10}(g) + Al_2Cl_6(g) = 2UCl_5 \cdot AlCl_3(g) \quad (17)$$

to be

$$\Delta F = 2696 - 6.10T \text{ cal/mol} \quad (18)$$

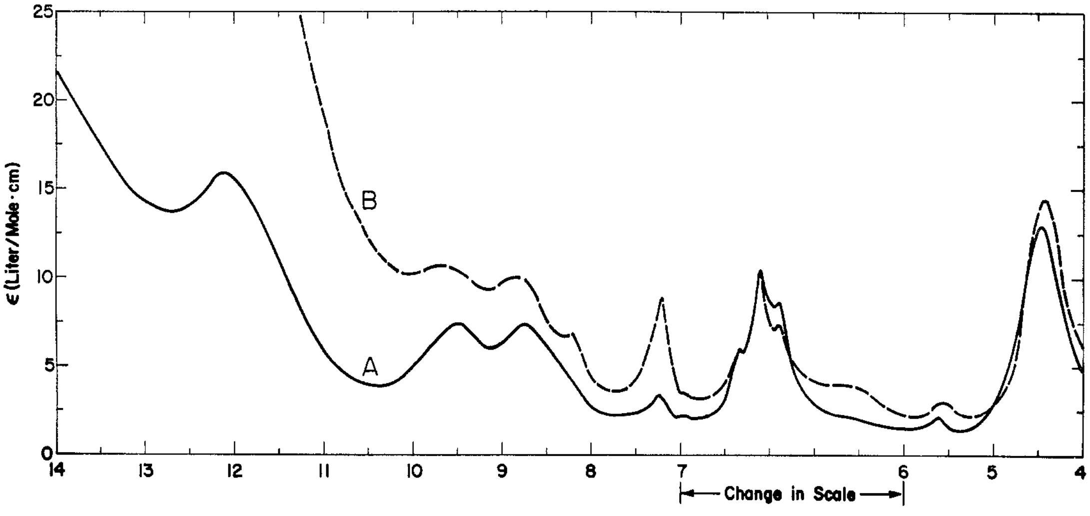

Figure 6.—"High-temperature" spectra of uranium pentachloride: A, UCl_4–$AlCl_3$–Cl_2 system at 852°K; B, UCl_4–Cl_2 system at 844°K.

The small enthalpy of the gas-phase reaction between the U_2Cl_{10} dimer and the Al_2Cl_6 dimer to form the $UCl_5 \cdot AlCl_3$ complex indicates that the metal–halogen bond energies are only slightly affected in forming the complex. This circumstance in turn could be responsible for the small changes in vibrational frequencies to which attention has been called.

Equation 18 allows one to calculate the U_2Cl_{10} partial pressure in equilibrium with $UCl_5 \cdot AlCl_3$. It turns out that in the present series of measurements there was at most 2% U_2Cl_{10} in equilibrium with $UCl_5 \cdot AlCl_3$.

Although eq 18 predicts diminishing dimer pressures at higher temperatures, the "high-temperature" spectrum of the complex increasingly resembles the "high-temperature" uranium pentachloride spectrum as illustrated in Figure 6.

With increasing temperature, the dissociative equilibrium (eq 10) becomes more important so that a maximum in the partial pressure of the complex is to be expected. It appears then that at the higher temperatures (>800°K) a new species (possibly $UCl_5(g)$) becomes the predominating one, both in the presence and in the absence of aluminum chloride.

Uranium Tetrachloride–Aluminum Chloride Vapor Complex.—In earlier work,[3] the reaction

$$n_1UCl_4(s) + n_2Al_2Cl_6(g) = UAl_{2n_2}Cl_{4n_1+6n_2}(g) \qquad (19)$$

was studied over a very limited range of Al_2Cl_6 pressures. The considerable volatility of the uranium tetrachloride–aluminum chloride complex was demonstrated in that work but the data could not be used to establish the stoichiometry and the thermodynamics of reaction 19.

The present series of measurements was performed over a range of Al_2Cl_6 pressures varying from 0.8 to 5 atm at temperatures from 600 to 800°K. The data listed in Table IV are for temperatures at which all of the $AlCl_3$ added to an optical cell is in the vapor phase. Under the conditions employed in these experiments, UCl_4 appears not to form a solid compound with $AlCl_3$ so that all of the data points refer to equilibrium 19. The amounts of UCl_4 and $AlCl_3$ in each experiment, cell volumes, and cell path lengths are listed in Table IV. Furthermore, Table IV gives $\bar{T}$, $T_{\min}$, P^0, the ideal gas law pressure of Al_2Cl_6, P', the Al_2Cl_6 pressure corrected for the dissociative equilibrium (eq 10), P, the Al_2Cl_6 pressure corrected for consumption by complex formation, the absorbance at 8734 cm^{-1}, and finally the pressure of the U(IV)–Al–Cl complex calculated using eq 2.

In a separate experiment, the molar absorptivity of the complex was determined by measuring, as a function of temperature, the absorbance of a cell to which 4.5 mg of UCl_4 and 0.58 g of $AlCl_3$ had been added. The plot of absorbance at 8734 cm^{-1}, the maximum of the most intense band of the complex, *vs.* temperature attained zero slope at 625°K and remained constant up to 870°K. It was concluded that all of the UCl_4 initially added to the cell had vaporized as complex at 625°K. From these data one calculates $\epsilon_{8734\ cm^{-1}} = 25.9$.

The absorption spectrum of the complex at 845°K is shown in Figure 7B together with the spectrum of UCl_4 vapor (Figure 7A) measured at 1225°K. At 8734 cm^{-1}, the molar absorptivity of $UCl_4(g)$ is 5.5. At 700°K, the vapor pressure of UCl_4 is 3×10^{-2} mm while in a typical experiment, the vapor pressure of the complex is 30 mm. The contribution of $UCl_4(g)$ to the measured absorbance at 8734 cm^{-1} therefore is less than 0.1% and can be neglected.

In order to determine n_2 in reaction 19, equilibrium quotients K were calculated for n_2 = 0.5, 1, 1.5, and 2. Log K's were plotted *vs.* $1/T_{\min}$ and least-squares lines were determined for all of the data points. The sums of the squared deviations were 0.234, 0.106, 0.758, and 2.32, respectively, for the n_2 values listed above. Only the graph for $n_2 = 1$ is reproduced (Figure 8) since this model represents the best fit of the data. The data are therefore well represented in terms of the reaction

$$UCl_4(s) + Al_2Cl_6(g) = UCl_4 \cdot Al_2Cl_6(g) \qquad (20)$$

Table IV

Data for the Reaction

$n_1UCl_4(s) + n_2Al_2Cl_6(g) = U_n\,Al_{2n_2}Cl_{4n_1+6n_2}(g)$

Conditions	T_{min}, °K	$\overline{T}$, °K	Pressures at $\overline{T}$, mm $P^0_{Al_2Cl_6}$	$P'_{Al_2Cl_6}$	$P_{Al_2Cl_6}$	$P_{U(IV)-Al-Cl}$ complex	Absorbance
Expt 20E	593.5	598	1308	1298	1292	5.19	0.070
$W_{UCl_4} = 0.1319$ g	653.2	659	1441	1410	1394	14.54	0.178
$W_{Al_2Cl_6} = 0.5197$ g	701.5	707	1546	1478	1449	29.80	0.340
$V = 55.54$ ml	752.1	756	1653	1521	1450	73.09	0.780
$l = 19.41$ cm	807.1	808	1767	1522	1382	152.24	1.520
	839.7	840	1837	1497	1315	203.04	1.950
Expt 25E	636.0	642	3359	3323	3289	32.75	0.215
$W_{UCl_4} = 0.1081$ g	675.2	681	3563	3493	3432	62.05	0.384
$W_{Al_2Cl_6} = 0.6440$ g	710.7	716	3746	3626	3533	94.29	0.555
$V = 28.76$ ml	731.4	736	3851	3692	3558	136.56	0.782
$l = 10.14$ cm	756.8	760	3977	3758	3562	201.97	1.120
	786.6	788	4123	3815	3539	286.06	1.530
Expt 26E	673.6	679	694	664	651	12.78	0.078
$W_{UCl_4} = 0.1079$ g	718.2	723	739	681	657	25.83	0.148
$W_{Al_2Cl_6} = 0.1290$ g	764.3	767	784	682	634	51.47	0.278
$V = 29.50$ ml	865.3	866	885	605	463	176.84	0.846
$l = 9.97$ cm							

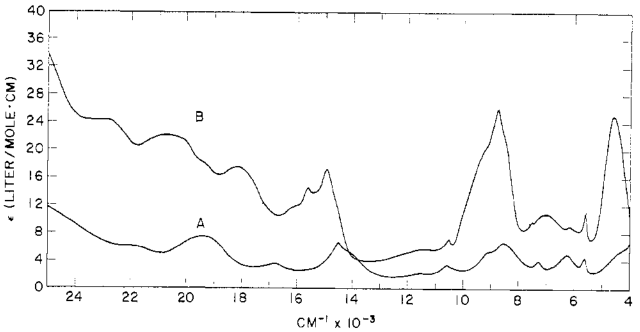

Figure 7.—Absorption spectra of gaseous UCl_4 at 1225°K (A) and of gaseous $UCl_2(AlCl_4)_2$ at 845°K (B).

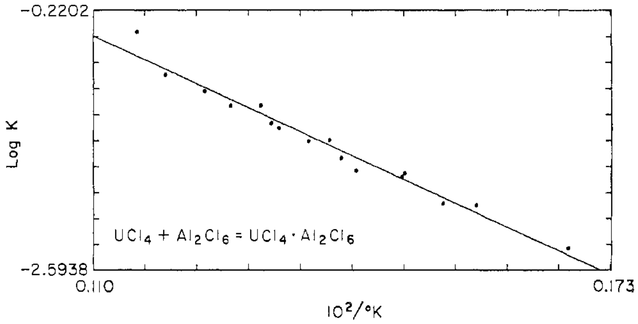

Figure 8.—Plot of log K vs. $1/T_{min}$ for reaction 20.

The free energy of this reaction is given by

$$\Delta F = 15{,}780 - 15.30T \text{ cal/mol} \qquad (21)$$

It should be noted that K for this reaction is dimensionless. The partial pressure of the complex can be expressed by the equation

$$\log P_{U(IV)-Al-Cl} = -\frac{3450}{T} + 3.34 + \log P_{Al_2Cl_6} \qquad (22)$$

Using $\Delta F = -47{,}700 + 47.6T$ for the reaction[6]

$$UCl_4(g) = UCl_4(s) \qquad (23)$$

and ΔF for reaction 20, one calculates ΔF for the reaction

$$UCl_4(g) + Al_2Cl_6(g) = UCl_4 \cdot Al_2Cl_6(g) \qquad (24)$$

to be $-31{,}920 + 32.3T$ cal/mol.

The large negative enthalpy of this gas-phase reaction can be rationalized in terms of generalized acid–base considerations. From this viewpoint, $UCl_4(g)$ is a relatively good electron-donor molecule *vis à vis* Al_2Cl_6. Although supporting spectroscopic data are lacking, we propose that the complex molecule be formulated as $UCl_2(AlCl_4)_2$ to indicate the transfer of two chlorides from UCl_4 to form two $[AlCl_4]$ groups.

It is instructive to compare the volatility of the uranium tetrachloride–aluminum chloride complex in the presence of 1 atm of Al_2Cl_6 to the volatility of pure UCl_4. Using eq 22 and the known vapor pressure equation[6] of solid UCl_4, one obtains for the volatility ratio $P_{UCl_2(AlCl_4)_2}/P_{UCl_4}$

$$\log V_r = \frac{6980}{T} - 7.1 \qquad (25)$$

Typical V_r values are ~10^7 (500°K), ~10^4 (600°K), ~10^3 (700°K), and ~10^2 (800°K). It is noteworthy that the vapor pressure of the complex at 600°K in the presence of 1 atm of Al_2Cl_6 is 0.4 mm. Since UCl_4 does not appear to form a solid complex with $AlCl_3$, transport of UCl_4 in a stream of $Al_2Cl_6(g)$ should occur at temperatures as low as 600°K.

Experimental Section

$AlCl_3$ was prepared by passing HCl over analytical grade Al wire (<10^{-6} ppm total impurities, Cominco Products, Inc., Spokane, Wash.) at about 500°K. The HCl, produced by treating NaCl with H_2SO_4, was dried by passage through an acetone–Dry Ice trap. The $AlCl_3$ was sublimed in an HCl atmosphere and HCl was pumped off under vacuum. UCl_4 (Special Materials, ANL) was sublimed at 800°K in an N_2 stream saturated with CCl_4. The sublimate was stored in an evacuated container. Chlorine gas (99.965% minimum purity, The Matheson Co., Inc., Joliet, Ill.) was condensed in the optical cells using liquid

N_2. UCl_4 and $AlCl_3$ were weighed out on a microbalance and transferred to an optical cell in a helium drybox whose water content was <3 ppm.

In order to permit spectral measurements to be made over as large a temperature and pressure interval as possible, heavy-walled cylindrical cells (wall thickness 2–3 mm) and 10- or 20-cm path lengths were used, with volumes ranging between 30 and 75 cm^3. The cells were fabricated from quartz tubes by fusing 3-mm thick quartz windows on the ends making sure that the entire window thickness was employed in making the seal. Several cells ruptured before this procedure in making the seals was adopted. Cell volumes were determined to within 0.2% by pycnometric weighing and the path length was measured with a caliper to ±0.03 cm. The cells, after addition of measured amounts of UCl_4, Al_2Cl_6, and Cl_2 gas, were sealed off under vacuum at the side arm.

The cells were placed in a cylindrical furnace of a type previously described.[29] Spectra were generally measured in the temperature range 400–700°K and total pressures of 1–5 atm.

In order to prevent condensation of $AlCl_3$ or UCl_4 on the windows and to minimize heat losses, small auxiliary Pt heaters were placed in both end portions of the furnace and the ends of the furnace were fitted with outer quartz windows. The voltage of the Pt heaters was kept constant over a run. With this arrangement, the temperature at the cell windows was about 40° higher than the middle of the cell at 500°K and only a few degrees higher at 800°K. Calibration curves for the temperature distribution along the cells were obtained as a function of temperature with a dummy cell in the furnace. In order to vary the position of the thermocouple within the cell, a small hole was drilled through the furnace and cell windows. Heat losses were found to be somewhat less during an actual run so that the average temperatures T, determined in the calibration runs, are estimated to be within 5° of the actual temperature.

During the runs, the temperature was measured with the thermocouple situated near the middle of the furnace adjacent to the cells. It was found that this temperature was within ±0.5° of the minimum temperature $T_{\min}$, measured inside the cell during a calibration run.

A Cary 14 H spectrophotometer with the sequence: light source → chopper → sample → monochromator → detector → ac amplifier → recorder was used for the spectral measurements. The usefulness of this arrangement for high-temperature measurements has been described elsewhere.[30]

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(29) D. M. Gruen and C. W. DeKock, *J. Chem. Phys.*, **45**, 455 (1966).

(30) D. M. Gruen, *Quart. Rev.* (London), **19**, 349 (1965).

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Kinetics and Mechanism of the Oxidation of Vanadium(II) by Vanadium(V) in Aqueous Perchlorate Solutions[1a]

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The reaction of V^{2+} and VO_2^+ in perchloric acid solution occurs mainly to produce V^{3+} and VO^{2+}, although both the rate and stoichiometry are affected to some extent by a side reaction between V^{3+} and VO_2^+. After correction for that effect, the main reaction was found to follow the rate expression $-d[VO_2^+]/dt = \{a + b[H^+]\}[V^{2+}][VO_2^+]$. At $\mu = 1.00\ M$ and 25.0°, $10^{-3}a = 2.58 \pm 0.10\ M^{-1}\ sec^{-1}$ and $10^{-3}b = 2.16 \pm 0.15\ M^{-2}\ sec^{-1}$. The rate constants were evaluated at other temperatures giving the following activation parameters: $\Delta H_a^{\ddagger} = 1.9 \pm 0.4$ kcal mol^{-1}, $\Delta S_a^{\ddagger} = -36.8 \pm 1.4$ eu, $\Delta H_b^{\ddagger} = 1.8 \pm 0.9$ kcal mol^{-1}, and $\Delta S_b^{\ddagger} = -37.3 \pm 3.1$ eu. The reaction was also studied in the presence of thiocyanate ion; very rapid oxidation of $VNCS^+$ to $VNCS^{2+}$ by VO_2^+ was noted with a rate constant of $(4 \pm 1) \times 10^5\ M^{-1}\ sec^{-1}$. Possible reaction mechanisms are discussed.

Introduction

Vanadium is known in four oxidation states in acidic aqueous solution, representing oxidation numbers +2 through +5. Each of the ions $V(H_2O)_6^{2+}$, $V(H_2O)_6^{3+}$, VO^{2+}, and VO_2^+ is stable with respect to disproportionation since the ions become uniformly better oxidizing agents as the oxidation state increases.[2] The lower two ions must be protected from oxygen oxidation,[3,4] and both reduce perchlorate ion at appreciable rates,[5] rendering them metastable with respect to oxidation by the perchlorate salts that usually constitute the preferred reaction media.

The rates of the electron-exchange reactions of adjacent ions have been measured: V^{2+} and V^{3+},[6] V^{3+} and VO^{2+},[7] and VO^{2+} and VO_2^+.[8] The net reactions between oxidation states differing by two electrons have also been studied: the conversion of V^{2+} and VO^{2+} to V^{3+}, which occurs in part by way of the unstable intermediate VOV^{4+},[9] and the reaction of V^{3+} and VO_2^+ to form VO^{2+}.[10]

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(1) (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2599. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

(2) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952.

(3) J. B. Ramsey, R. Sugimoto, and H. DeVorkin, *J. Am. Chem. Soc.*, **63**, 3480 (1941).

(4) J. H. Swinehart, *Inorg. Chem.*, **4**, 1069 (1965).

(5) W. R. King, Jr., and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

(6) K. V. Krishnamurty and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 592 (1958).

(7) S. C. Furman and C. S. Garner, *ibid.*, **74**, 2333 (1952).

(8) C. R. Guiliano and H. M. McConnell, *J. Inorg. Nucl. Chem.*, **9**, 171 (1959).

(9) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964); *Inorg. Chem.*, **3**, 569 (1964).

(10) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).