CONTRIBUTION FROM THE HANFORD LABORATORIES,
GENERAL ELECTRIC COMPANY, RICHLAND, WASHINGTON

Fused Salt Spectrophotometry. IV. Uranium(IV) in Chloride Melts[1]

BY JOHN R. MORREY

Received December 1, 1961

The absorption spectra of UCl_4 in several fused chloride solvents have been obtained at various temperatures over the range 300–2600 mμ. Comparison with spectra of pure molten and solid Cs_2UCl_6 clearly indicates that the hexachlorouranate(IV) ion occurs in all of these solvents except $ZnCl_2$ and is in equilibrium with another species in the alkali chlorides. The order of stability of UCl_6^{-2} in the various solvents is given by the sequence $CsCl–CsAlCl_4 = KCl–KAlCl_4 > CsCl > KCl > NaCl > ZnCl_2$. At least one different species occurs in $ZnCl_2$. Comparison with spectra of UCl_4 in the pure molten and solid states provides evidence that all the uranium species detected have a coördination number of six or less. The spectra of U(IV) in $CsCl–AlCl_3$ and $KCl–AlCl_3$ are identical at a given $MCl/AlCl_3$ ratio, but both vary as the ratio varies; they change markedly at the composition corresponding to $MAlCl_4$. Equilibria involving complex ions which account for this phenomenon are proposed. Temperature dependence of spectra also is discussed.

Introduction

Spectra of UCl_4 in fused LiCl–KCl eutectic and pyridinium chloride have been reported previously by Gruen and McBeth.[2] The species present in pyridinium chloride was identified as UCl_6^{-2} by comparison of its spectrum with that of U(IV) in single crystals of $[(CH_3)_4N]_2UCl_6$ and Cs_2UCl_6, where an octahedral field is imposed on the U(IV) ion.[3,4] The spectrum of U(IV) in LiCl–KCl eutectic, being considerably different, was attributed to an octacoördinated complex species.

Our investigation explores in more detail the relationships between the nature of the fused chloride solvent and the complex U(IV) ions produced. It was first undertaken to determine whether fused chloride media produced significantly different complex ions and consequently whether oxidation–reduction data of actinides in a particular alkali chloride could be extended to other alkali chlorides without serious errors.[5] That such complex ions have been found provides evidence that thermodynamic extensions cannot be made with confidence in U(IV) systems. A subsequent paper will establish the same results for U(III).

Experimental

Materials.—The NaCl, KCl, and $ZnCl_2$ were, respectively, Baker and Adamson reagent, reagent special, and reagent grade. The CsCl was Fairmont reagent grade. All of these materials were dried by first bubbling chlorine, then oxygen-free argon, through the melts. While still hot, the salts were transferred to a drybox having a water partial pressure of about 3×10^{-2} mm.

The UCl_4 was prepared by refluxing 50 g. of pre-dried UO_3 in 100 ml. of hexachloropropene. The resulting finely divided precipitate was washed several times with CCl_4, transferred as a slurry into a quartz tube, and slowly evacuated while the temperature was gradually raised to 400°. The container then was filled with spectroscopic grade argon to about 15 mm. pressure. The temperature subsequently was increased to about 600°, thus allowing the UCl_4 to fractionate and produce large, well formed crystals outside the heated zone.

Baker and Adamson C.P. grade anhydrous $AlCl_3$ was sublimed at about 170° under a pressure of about 15 mm. of dry argon. The sublimate sometimes was yellow, suggesting that ferric chloride was an impurity. However, spectrographic analysis indicated that less than 0.01% iron was present. Frequently, when $AlCl_3$ was mixed with KCl or CsCl and melted under vacuum, a black, carbonaceous precipitate was formed which is believed to have come from the decomposition of an organic material having about the same vapor pressure as $AlCl_3$. A clear solution suitable for spectrophotometric work was obtained by digesting the precipitate at 500° for a few hours, then filtering the solution under vacuum by carefully inverting the container, the two chambers of which were separated by a fine quartz frit.

Because of their hygroscopic nature, $AlCl_3$, UCl_4, and $ZnCl_2$ could be maintained in a drybox for only a short time. Zinc chloride had to be dried just prior to its use. The $AlCl_3$ and UCl_4 were stored in sealed ampoules which were opened just prior to their use.

Cesium hexachlorouranate(IV) was obtained from a 10 *M* HCl solution which was 0.082 *M* in CsCl and 0.041 *M* in UCl_4. Crystals were formed by allowing the solution to evaporate over $Mg(ClO_4)_2$ and NaOH in a desiccator under a nitrogen pressure of 20 mm.

Anal. Calcd. for Cs_2UCl_6: Cs, 37.1; U, 33.2; Cl, 29.7. Found: Cs, 37.01 ± 0.12; U, 33.9 ± 0.2; Cl, 28.9 ± 0.2.

The slight chloride deficiency can be attributed to about 5% $Cs_2UO_2Cl_4$. However, this compound does not absorb above about 500 mμ and therefore does not contribute significantly to the spectrum.

Apparatus.—A Cary Model 14 or 14H spectrophotometer was used in these studies. A description of the sample and reference furnaces for the Model 14 and a discussion of errors related to high temperature spectrophotometry appear in other publications.[6,7] Fused quartz cuvettes outfitted with quartz fittings were used as containers. Quartz frits sometimes were included to filter the molten sample as it entered the cuvettes.

Procedure.—The appropriate materials were weighed in the drybox, placed in cuvettes, and immediately evacuated. Since some physical adsorption of gases occurred during manipulation of materials in the drybox, the cuvettes were heated during the evacuation prior to being sealed. All samples which did not

---

[1] Work performed under Contract No. AT(45-1-)-1350 for the U. S. Atomic Energy Commission.

[2] D. M. Gruen and R. L. McBeth, *J. Inorg. Nucl. Chem.*, **9**, 290 (1959).

[3] (a) S. Siegel, *Acta Cryst.*, **9**, 827 (1956); (b) W. H. Zachariasen, *ibid.*, **1**, 268 (1948).

[4] E. Staritzky and J. Singer, *ibid.*, **5**, 536 (1952).

[5] In the case of uranium(III), several such studies in LiCl–KCl eutectic have been reported: D. M. Gruen and R. A. Osteryoung, *Ann. N. Y. Acad. Sci.*, **79**, 897 (1960); D. L. Hill, J. Perano, and R. A. Osteryoung, *J. Electrochem. Soc.*, **107**, 698 (1960); D. Inman, G. J. Hills, L. Young, and J. O'M. Bockris, *Trans. Faraday Soc.*, **55**, 1904 (1959); S. N. Flengas, *Can. J. Chem.*, **39**, 773 (1961); D. Inman and J. O'M. Bockris, *ibid.*, **39**, 1161 (1961).

[6] J. R. Morrey and A. W. Madsen, *Rev. Sci. Instr.*, **32**, 799 (1961).

[7] J. R. Morrey and E. E. Volland, *Spectrochim. Acta*, to be published.

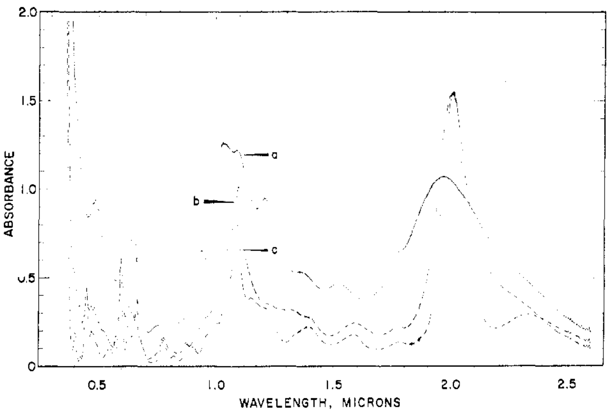

Fig. 1.—Effect of KCl/AlCl$_3$ mole ratio on the spectrum of U(IV): (a) KCl/AlCl$_3$ = 0.802, 0.0884 *M;* (b) KCl/AlCl$_3$ = 1.008, 0.0855 *M;* (c) KCl/AlCl$_3$ = 1.047, 0.0823 *M;* T = 450°, cell width = 1.00 cm.

contain AlCl$_3$ were heated to near their melting point. Those containing AlCl$_3$ were held at 60° for 1 hr. before being sealed. This allowed sufficient desorption provided no hydrolysis had taken place previously.

In spite of the precautions employed during sample preparation, an orange film, believed to be UO$_3$, developed initially in U(IV)–alkali chloride solutions at 650° and permanently damaged the cuvette. This problem was overcome by holding the salts for several hours in the tube attached to the cuvette at a temperature above that at which the spectrum was to be obtained. Only after film formation had ceased were the salts introduced to the cuvette.

Whenever temperature was critical, it was controlled to within $\pm 0.5°$.

As the cuvettes were removed from the spectrophotometer, they were inverted before the sample solidified to avoid damaging the cuvette. After the spectra had been obtained, samples of salts were analyzed chemically to confirm the make-up composition. All spectra were obtained repeatedly to ensure that no change occurred with time.

Although precautions were taken to avoid contamination by moisture during the preparation of KCl–AlCl$_3$, there was some indication that there were present trace amounts of water or oxide since at temperatures above 600° a cloudiness appeared which caused light scattering at the shorter wave lengths. It is believed that the cloudiness was due to the formation of finely divided Al$_2$O$_3$. It has been reported that the aluminum hydroxy-oxide, diaspore, is stable to 450° and that Al$_2$O$_3$ is stable above this temperature.[8] Since there may be some modification of the stabilities of these compounds in a melt of KCl–AlCl$_3$, it is quite possible that small quantities of soluble diaspore existed in the melt to 600°, at which temperature it formed an exceedingly fine precipitate of Al$_2$O$_3$.[9]

Results and Discussion

U(IV) in KCl–AlCl$_3$ Solutions.—Distribution studies involving U(III) in a molten KCl–AlCl$_3$–Al system revealed a strong dependence of the activity of U(III) on the mole ratio of KCl to AlCl$_3$.[10,11] This behavior was successfully attributed to competitive reactions involving complex ions. Similarly, U(IV) in the same solvent was expected to form complex ions and, by analogy to aqueous systems, the different coördination species formed were expected to exhibit different absorption spectra. Spectrophotometric changes shown in Fig. 1 verify the marked environmental effect on the spectrum of U(IV) over the compositional range of $0.80 \leq \text{KCl/AlCl}_3 \leq 1.043$. Competitive reactions involving complex ions can adequately describe these results, *viz.*

$$\text{Cl}^- + \text{AlCl}_3 \underset{}{\overset{K_1}{\rightleftharpoons}} \text{AlCl}_4^- \qquad (1)$$

$$6\text{Cl}^- + \text{U(AlCl}_4)_x{}^{4-x} \overset{K_2}{\rightleftharpoons} x\text{AlCl}_4^- + \text{UCl}_6^{-2} \qquad (2)$$

Since K_1 is much larger than K_2,[11] UCl$_6^{-2}$ will not form when KCl/AlCl$_3$ < 1 because the buffer pair AlCl$_3$–AlCl$_4^-$ strongly lowers the chloride activity. However, when KCl/AlCl$_3$ > 1 (KCl–KAlCl$_4$), UCl$_6^{-2}$ is allowed to form. The uranium concentration in the above samples was small enough that only a slight excess of KCl [KCl/AlCl$_3$ = 1.023] would supply enough chloride for complete formation of UCl$_6^{-2}$ provided K_2 were large. The constant K_2 has been shown to be about 7×10^4 in the case of U(III).[11] It is expected to be still larger for U(IV). Thus larger ratios should not affect the spectrum significantly. This has been verified; the spectrum does not change over the concentration range examined ($1.043 \leq \text{KCl/AlCl}_3 \leq 1.34$) The same observations also hold for the solvent CsCl–AlCl$_3$; whether the cation is potassium or cesium makes little difference.

The UCl$_6^{-2}$ ion was identified in molten KCl–KAlCl$_4$–UCl$_4$ and CsCl–CsAlCl$_4$–UCl$_4$ by comparing the spectra with that of molten Cs$_2$UCl$_6$. From Fig. 2g and 3c-3 and Table I it can be seen that the spectra are almost identical.

The small differences can be attributed to effects of external environment on the complex ion. The spectrum of U(IV) in CsCl is very similar to that of U(IV) in Cs$_2$UCl$_6$ or KCl–KAlCl$_4$. Nevertheless, from examination of the region 1100 to 1150 mμ and comparison of the absorbance ratio A_{1100}/A_{1150} of CsCl with the same ratio for NaCl, it is evident that CsCl contains a small amount of the same species as is contained in NaCl in much larger proportions. The identity of this species, species A, will be discussed later.

The existence of temperature-induced isosbestic points shown in Fig. 3c virtually guarantees that there is very little of any other species present in MCl–MAlCl$_4$ and therefore in Cs$_2$UCl$_6$. Ordinarily, the occurrence of isosbestic points is proof that only two species change relative concentration in the system. However, the conventional argument requires that the

---

[8] A. W. Laubengayer and R. S. Weisz, *J. Am. Chem. Soc.*, **65**, 247 (1943).

[9] In the study of UCl$_3$ in KCl–AlCl$_3$, when the temperature was raised above 600°, some of the U(III) occasionally oxidized to U(IV) simultaneously with the formation of a fine light-scattering precipitate. Subsequent temperature variation above and below 600° revealed a reversible equilibrium which has been attributed to the reactions

$$2\text{AlOOH} \longrightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$$

$$3/2\ \text{H}_2\text{O} + \text{AlCl}_3 \longrightarrow 1/2\ \text{Al}_2\text{CO}_3 + 3\text{HCl}$$

$$\text{HCl} + \text{UCl}_3 \rightleftharpoons \text{UCl}_4 + 1/2\ \text{H}_2$$

[10] R. H. Moore, J. R. Morrey, and E. E. Voiland, *J. Phys. Chem.*, in press.

[11] J. R. Morrey and R. H. Moore, *ibid.*, in press.

TABLE I

COMPARISON OF ABSORPTION PEAKS COMMON TO UCl_6^{-2} FOR U(IV) IN VARIOUS MEDIA

		Absorbance at wave lengths (Wave lengths in mμ)					Absorbance ratios			
Medium	Temp., °C.	600 (a)	668 (b)	1100 (c)	1150 (d)	2020 (e)	b/a	b/c	c/d	c/e
KCl–$KAlCl_4$	700	0.398	0.363	0.689	0.503	1.018	0.91	0.53	1.37	0.68
Cs_2UCl_6	700	.212	.175	.292	.207	.525	.83	.60	1.41	.56
CsCl	700	.250	.240	.351	.325	.522	.96	.68	1.08	.67
NaCl	825	.520	.631	.549	.590	.535	1.21	1.14	0.93	1.03

total concentration of absorbing species remain constant, a condition not satisfied because of solvent expansion when the temperature is increased. Over the temperature range of Fig. 3c the solvent expands about 9%. In this case, it can be shown that isosbestic points indicate appreciable absorbance by only UCl_6^{-2} at the wave length of each isosbestic point and that UCl_6^{-2} does not undergo an appreciable equilibrium change with temperature.[12] Table II summarizes in detail the temperature dependence of this system. All peaks but the one at 670 mμ shifted to lower energies with temperature. In each of these cases, the shift was about 0.1 Å./°C.

The spectrum of U(IV) in chloride-deficient solvent (Fig. 1a, b) is highly temperature dependent, as is indicated in Fig. 3a.

As the temperature is increased, all the peaks are attenuated more than can be accounted for on the basis of dilution, broadening, or emission.[7,12] It also is evident that a change in temperature effects a change in the relative amounts of at least two species in the melt. The species exhibiting the predominant spectrum at lower temperatures is characterized by strong peaks at 625, 1040, 1210, and 1900 mμ. As the temperature is raised, peaks at 670, 1100, and 2000 mμ become more evident. It thus appears that a relatively weak complex gives rise to the low-temperature spectrum which is not due to a simple mixture of species found in any of the other systems investigated. Nevertheless, at high temperatures the spectrum changes in a manner reminiscent of formation of the species found in $ZnCl_2$ (to be discussed later). Since the peak at about 625 mμ, which appears to be associated with octahedral fields, diminishes with temperature, it might indicate the conversion of $U(AlCl_4)_6^{-2}$ to $U(AlCl_4)_4$.

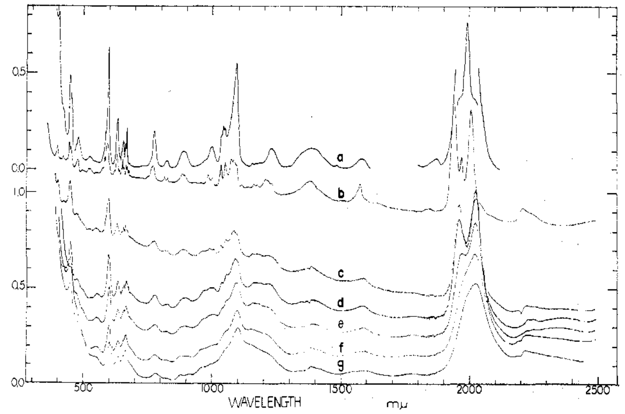

Fig. 2.—UCl_6^{-2} in molten and solid Cs_2UCl_6 and $[(n\text{-}C_8H_{17})_3NH]_2UCl_6$: (a) $[(n\text{-}C_8H_{17})_3NH]_2UCl_6$, 0.06 *M* in xylene at 25°, cell width 1.00 cm.; (b), (c), (d), (e) Cs_2UCl_6 at 25, 400, 500, and 615°, respectively, cell width 0.0098 cm., solid state, some light scatter at shorter wave lengths; (f), (g) Cs_2UCl_6 at 650 and 700°, respectively, cell width 0.0098 cm., liquid state.

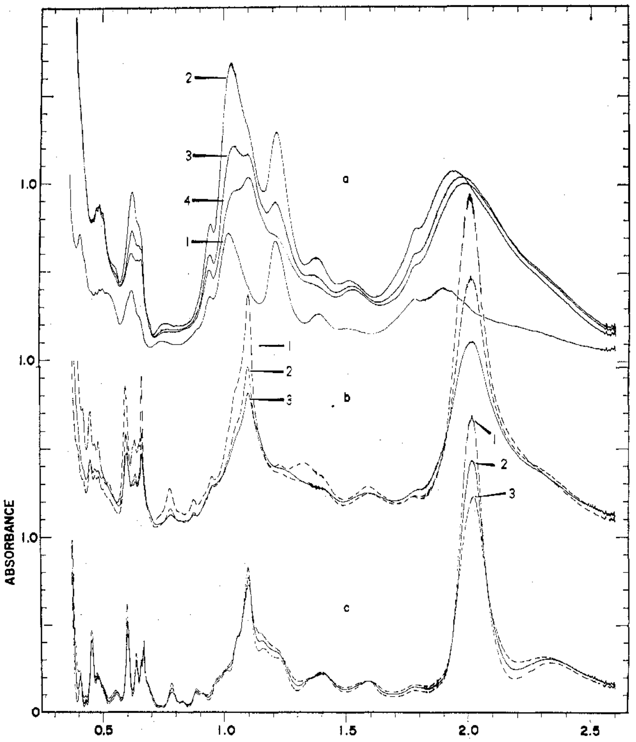

Fig. 3.—Effect of temperature on the spectrum of U(IV) in various KCl–$AlCl_3$ compositions. (a) KCl/$AlCl_3$ = 0.806: (1) 250°, saturated in UCl_4; (2) 350°, supersaturated in UCl_4; (3) 450°; (4) 550°. (b) KCl/$AlCl_3$ = 1.008: (1) 300°; (2) 500°; (3) 700°. (c) KCl/$AlCl_3$ = 1.047: (1) 400°; (2) 500°; (3) 700°. In all cases the cell width is 1.00 cm. Mole fractions are based on UCl_4, KCl, and $AlCl_3$ as entities: (a) (1) $X = 1.8 \times 10^{-3}$; (2, 3, 4) $X = 5.68 \times 10^{-3}$; (b) $X = 5.69 \times 10^{-3}$; (c) $X = 5.44 \times 10^{-3}$.

Cation Effects.—Figure 4 compares spectra of UCl_4 in molten NaCl, KCl, and CsCl at the same temperature and virtually the same concentrations. Since reliable density data for the pure molten alkali chlorides are available, the volume-molal concentrations can be calculated and are approximately the molar concentrations.[13–16] The spectra show that at

---

[12] J. R. Morrey, *J. Phys. Chem.*, **66**, 2169 (1962).

[13] F. M. Jaeger, *Z. anorg. allgem. Chem.*, **101**, 1 (1917).

[14] I. S. Jaffe and E. R. Van Artsdalen, *J. Phys. Chem.*, **60**, 1125 (1956).

[15] J. D. Edwards, C. S. Taylor, *et al.*, *J. Electrochem. Soc.*, **99**, 527 (1952).

[16] R. W. Huber, E. V. Potter, and H. W. St. Clair, U. S. Bur. Mines Rept. No. 4858, 1952.

TABLE II

TEMPERATURE EFFECTS ON SPECTRUM OF THE KCl–AlCl$_3$–UCl$_4$ SYSTEM (FIG. 3c)

Wave length of maximum absorbance, mμ					Associated isosbestic points,[a] mμ	
400°	450°	500°	550°	600°	Right	Left
2015.5	2015.7	2017.5	2018.5	2019.5	2065	1921.8
1098.2	1099.0	1099.5	1100.0	1101.0	1108.9	1062.5
782.5	783.5	784.5	784.5	785.5	800.8	751.8
670.2	670.1	670.0	670.0	670.0	687.0	...
658.5	659.0	659.1	659.1	659.5	...	651.5
638.8	639.3	639.6	640.0	640.3	647.0	626.2
456.2	456.3	456.5	456.8	457.0	467.0	443.0

[a] Other isosbestic points: 1609.5; 1563.8; 1425.0; 1348.2; 1038.8; 920.0; 866.0; 840.0; 815.5 mμ.

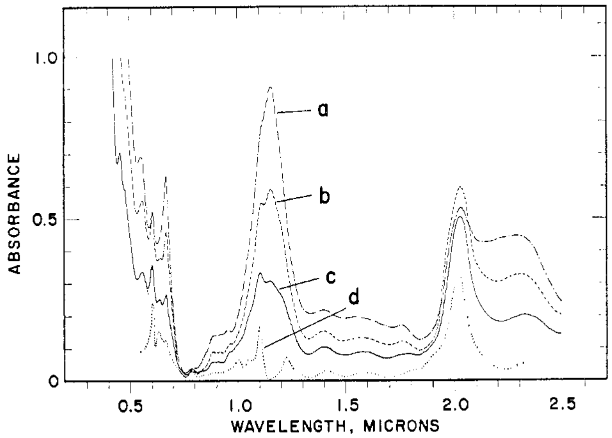

Fig. 4.—UCl$_4$ in molten alkali chlorides at 825°: (a) 0.181 *M* in NaCl; (b) 0.175 *M* in KCl; (c) 0.177 *M* in CsCl; (d) spectrum obtained from subtracting 0.34 of spectrum (a) from spectrum (c). Cell width in all cases, 0.200 cm.

least two species are present in various ratios. The species A, most apparent in NaCl, has a much stronger absorptivity than that prevalent in CsCl, and is identified by principal peaks at 2300, 1150, and 668 mμ. The other species, prevalent in CsCl, is identified by principal peaks at about 2020, 1100, 668, and 602 mμ with small peaks at 1400, 1575, and 1775 mμ. That it is UCl$_6^{-2}$ is confirmed by analogous principal peaks in Fig. 2g. Spectra of [(C$_2$H$_5$)$_4$N]$_2$UCl$_6$ in nitromethane and [(*n*-C$_8$H$_{17}$)$_3$NH]$_2$UCl$_6$ in xylene (Fig. 2a) also are available for comparison.[17,18] Their remarkable resemblance confirms the fact that the energy levels are for the most part due to the octahedral arrangement of the chloro ligands; external environment produces only a minor effect.[19]

Comparison of the spectrum of species A with that of solid UCl$_4$ at room temperature (Fig. 5a) disclosed certain similarities. However, because at room temperature the uranium ion is surrounded by an eightfold unsymmetric field[20] (the closest chloride neighbors are sufficiently distorted from a tetrahedron to allow exposure of uranium to four next-nearest chloride neighbors), it was felt that the spectrum of molten UCl$_4$ might compare better to that of A than would the spectrum of solid UCl$_4$. It seemed plausible that the inner complex sphere would form a more regular tetrahedron upon expansion of the crystal or upon melting. Consequently, several attempts were made to obtain the spectrum of molten UCl$_4$, but with only partial success. Due to a slow reaction with the silica cell, gas bubbles formed, viscosity increased, and, ultimately, sufficient pressure was generated to break the container.[21] Spectra were not of good quality; nevertheless, sufficient data were obtained to reveal a change in field symmetry. This is seen by comparing Fig. 5a with 5b. The change was caused by a solid–solid transition below 490°. No appreciable spectral change took place at the melting point.

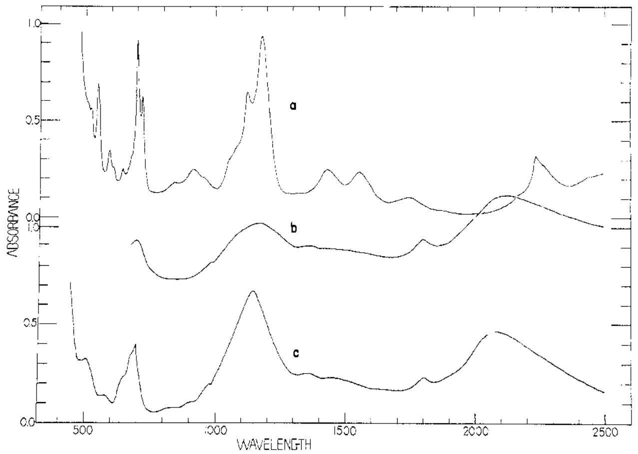

Fig. 5.—(a) Pure UCl$_4$ at 25°, cell width approximately 0.0013 cm.; (b) pure UCl$_4$ at 700° (because of experimental difficulties, relative absorbances are not reliable; those at shorter wave lengths generally are of greater intensity than indicated); (c) UCl$_4$ in ZnCl$_2$ at 575°, 0.0070 *M*, cell width 0.20 cm.

In a further effort to determine the spectrum of U(IV) in a tetrahedral field, the spectrum in molten ZnCl$_2$ was obtained because ZnCl$_2$ was expected to be a non-complexing medium for UCl$_4$ on the basis that Zn(II) and U(IV) have almost identical charge-to-surface ratios. Comparison of Fig. 5b with 5c strongly implies that the same field symmetry exists for U(IV) in molten UCl$_4$ as in molten ZnCl$_2$ at higher temperatures. However, although the spectra of U(IV) in ZnCl$_2$ and NaCl are similar in absorptivities and general peak shapes, they are sufficiently different to suggest the presence of another species.

Figures 1c, 2g, and 4b show that KCl–KAlCl$_4$ is more compatible to UCl$_6^{-2}$ formation than is KCl alone. The assumption that chloride ion activity in KCl is greater than that in KCl–KAlCl$_4$ would be consistent with the suggestion made by Gruen for the KCl–LiCl eutectic. One might conclude that species A, which is more prevalent in KCl, has a higher coördination number than six. This, however, is inconsistent with the condition predicted by charge-to-surface ratios of the alkali ions and the spectra of U(IV) in

---

[17] J. L. Ryan, *J. Phys. Chem.*, **65**, 1856 (1961).

[18] W. E Keder, J. L. Ryan, and A. S. Wilson, *J. Inorg. Nucl. Chem.*, **20**, 131 (1961).

[19] Other actinide species also seem to bear this out: see, for example, J. L. Ryan, *J. Phys. Chem.*, **64**, 1375 (1960); *ibid.*, **65**, 1099 (1961).

[20] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Part I, McGraw-Hill Book Co., New York, N. Y., 1951, p. 477.

[21] The reaction UCl$_4$(l) + SiO$_2$(s) $\rightarrow$ UO$_2$(soln) + SiCl$_4$(g) was confirmed by mass spectrometric identification of the gaseous product SiCl$_4$.

NaCl, KCl, and CsCl. The charge-to-surface ratios are in the order $Cs^+ < K^+ < Na^+$. The chloride ion activities in the corresponding chloride salts, along with the tendency to form complex ions, ought to be in the reverse order. There is substantial evidence from phase diagrams to confirm this. For example, it has been clearly shown that the tendency of UCl_4 to form complex compounds with alkali chlorides is in the order CsCl > RbCl > KCl > NaCl.[22] Magnesium chloride, $ZnCl_2$, and UCl_3 form complex compounds with alkali chlorides according to this order. Furthermore, distribution studies have shown $CsAlCl_4$ to be more stable than $KAlCl_4$.[23] Therefore, since CsCl allows the formation of more UCl_6^{-2} than do KCl or NaCl, species A should have a smaller coördination number than six because it is most concentrated in NaCl.

These conclusions also are consistent with the absorptivities of the various spectra reported in this paper. The absorption bands so far considered arise from f→f transitions which, to a certain degree, are forbidden. When the absorbing ion has a center of symmetry, this restriction is further enhanced. Accordingly, it is easy to explain why UCl_6^{-2} produces smaller absorptivities than species A and that found in $ZnCl_2$, provided the latter two have no center of symmetry; UCl_6^{-2} is centrosymmetric but the tetragonal structure is not.[24] These considerations are further illustrated in spectra of UCl_4 in aqueous solutions. Lower chloride complexes, which undoubtedly have mixed aquo-chloro ligands, have greater absorptivities by a factor of five than does UCl_6^{-2}. It is noteworthy, but not surprising, that the higher chloro complexes of U(IV) have not been detected in aqueous or organic solvents. The large negative charge, along with the steric effects, must seriously impair their stability. The ionic radius ratio of $U(IV)/Cl^-$, being 0.52 ± 0.02, is much too small for a coördination number of eight, the radius ratio of which should be above 0.73. On the other hand, a coördination number of six or less can be accommodated easily.

The anomalous tendency of UCl_6^{-2} to form with greater ease in solutions containing aluminum chloride than in pure alkali chlorides must be attributed to the large free energy of formation of $AlCl_4^-$. It appears that it is sufficient to overcome the ordering of the alkali chloride liquid structure, *i.e.*, the pseudo-crystal structure that remains in the alkali melt.[25] It appears that, as a consequence, the activity of the chloride ions is enhanced, thus allowing the formation of more UCl_6^{-2}.

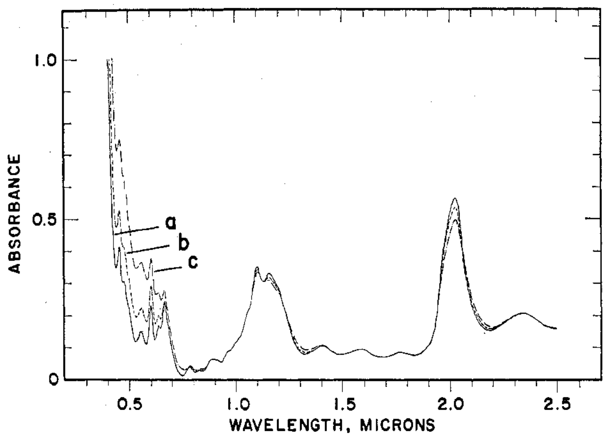

Fig. 6.—Effect of temperature on UCl_4 in CsCl: (a) 669°, 0.186 *M;* (b) 745°, 0.183 *M;* (c) 843°, 0.176 *M;* cell width 0.20 cm.

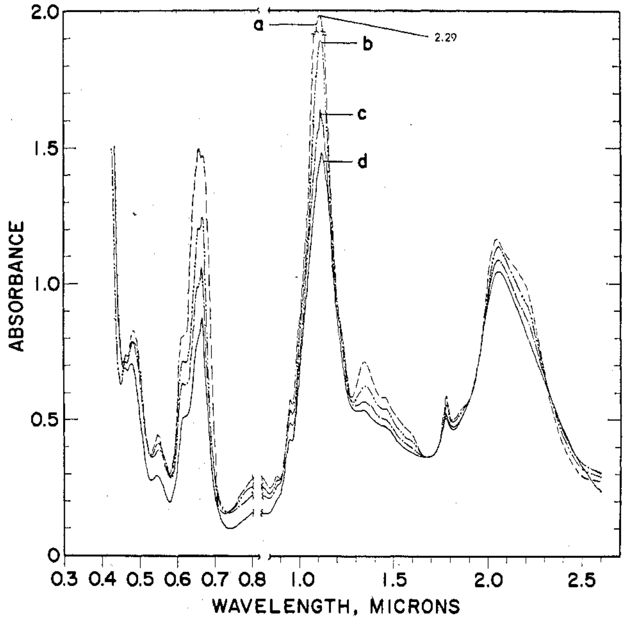

Fig. 7.—Effect of temperature on UCl_4 in $ZnCl_2$: (a) 304°, 0.078 *M;* (b) 400°, 0.076 *M;* (c) 500°, 0.075 *M;* (d) 575°, 0.073 *M;* cell width 1.00 cm.

The absorption of UCl_4 in CsCl below about 400 mμ, depicted in Fig. 6, probably is due to a charge transfer or f→d transition. As the temperature is raised, the edge of this intense band shifts to a longer wave length. At a given temperature this band is at a longer wave length for the NaCl system than for the CsCl system, indicating a lower energy transition for species A than for UCl_6^{-2}. The only other appreciable temperature effect in CsCl is the attenuation of all absorption peaks with increasing temperature—again more than can be attributed to the expansion of the solvent, broadening of the peaks, or emission errors.

Analogous studies on KCl or NaCl systems were not undertaken because of the high melting points of the solvents.

Figure 7 represents the effect of temperature on the spectrum of U(IV) in $ZnCl_2$. Qualitatively, it appears that an increase in temperature causes increased com-

---

[22] E. M. Levin and H. F. McMurdie, "Phase Diagrams for Ceramists," Part II, American Ceramic Society, 1959, pp. 81-85.

[23] R. H. Moore, private communication.

[24] Of the possible structures for octacoördination, two are centrosymmetric with respect to the central ion and two are not. The body-centered cubic and the rectangular face-centered trigonal prismatic structures are centrosymmetric; the dodecahedral and the Archimedean antiprismatic structures are not.

[25] This also appears to be borne out in the case of Cs_2UCl_6 and UCl_4 in excess CsCl. When sufficient U(IV) is present, it also appears to destroy the pseudo-crystal structure of the solvent; this cannot be accomplished with small concentrations of U(IV).

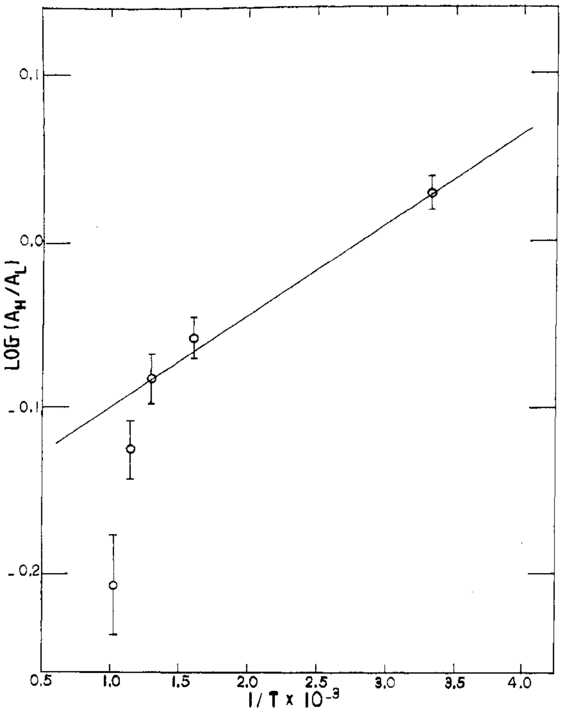

Fig. 8.—Theoretical and experimental absorbance ratios *vs.* temperature for vibronic peaks at 1946 and 2019 mμ.

plexation of U(IV), especially below 400°. At low temperatures the peak at 650 mμ is more prominent than that at 665 mμ but disappears at higher temperatures. The temperature dependence of complexation probably is dictated by the polymeric state of $ZnCl_2$ at the lower temperatures, as indicated by its viscous nature, and the dissociated state of $ZnCl_2$ at higher temperatures, where its viscosity decreases markedly.

Cesium Hexachlorouranate (IV).—Figure 2 provides a study of the temperature dependence of the spectrum of Cs_2UCl_6. Generally there is a gradual broadening as temperature is increased. One significant change, which is initiated by solidification, is the splitting of the rather intense peak at about 2000 mμ. Satten, Young, and Gruen's careful investigation of the absorption spectrum of Cs_2UCl_6 at low temperatures indicated that the spectrum is almost entirely vibronic in the visible and near-infrared.[26] The two peaks at 1946 and 2019 mμ were attributed to two vibronic transitions, 94 cm.$^{-1}$ on either side of the pure, forbidden electronic transitions at 1982 mμ. Normally the electronic peak is not detectable. However, it appeared in a rapidly quenched sample as can be examined in Fig. 2b. After several days at room temperature, the sample no longer exhibited this peak. Since pure electronic transitions are forbidden whenever there is a center of symmetry, this implies that some asymmetry was introduced as a result of strain.

The temperature-dependent absorbances of the two vibronic peaks at 1946 and 2019 mμ (hereafter referred to as H and L, respectively) can be attributed to a change in population of the various vibrational levels in the ground electronic state. Assuming that the population follows the Boltzmann distribution, we can calculate a theoretical absorbance ratio of the two vibronic transitions. Let N_0 be the concentration of absorbing molecules in electronic states (a) and (b), N_{ai} the concentration in the ith vibrational level of electronic state a, and N_{bj} the concentration in the jth level of electronic state b. Since $N_0 = \sum_{i=0} N_{ai} + \sum_{j=0} N_{bj}$, $N_{ai} = N_{a0} \exp(-i\epsilon_v/kT)$, and $N_{bj} = N_{a0} \exp[-(\epsilon_e + j\epsilon_v)/kT]$, where ϵ_e and ϵ_v are transitional energies for a → b and $i \rightarrow i + 1$, respectively, it follows that

$$N_{ai} = N_0 \exp(-i\epsilon_v/kT) \frac{1 - \exp(-\epsilon_v/kT)}{1 + \exp(-\epsilon_e/kT)} \text{[27]} \qquad (3)$$

The absorbance caused by a transition ai → bj is given by eq. 4 provided continuous emission is neglected

$$A_{ij} = \frac{h\nu_{ij}}{2.303c} B_{ai \rightarrow bj} N_{ai} L [1 - \exp\{-(\epsilon_e + (j - i))\epsilon_v/kT\}] \qquad (4)$$

where

A_{ij} = spectral absorbance due to the transition ai → bj
h = Planck's constant
$B_{ai \rightarrow bj}$ = induced transition probability for ai → bj
L = length of cell
c = speed of light
ν_{ij} = light frequency corresponding to the transition ai → bj[7]

Transitions H and L take place when $j = i + 1$ and $j = i - 1$, respectively. Thus, by substituting eq. 3 into 4, substituting C for $N_0hL/2.303c[(1 - \exp(-\epsilon_v/kT))]/[(1 + \exp(-\epsilon_e/kT))]$, and making the appropriate summations, expressions for the absorbances A_H and A_L are obtained

$$A_H = C\nu_H\{1 - \exp[-(_e + \epsilon_v)/kT]\} \sum_{i=0} B_{ai \rightarrow bi+1} \exp(-i\epsilon_v/kT) \qquad (5)$$

and

$$A_L = C\nu_L\{1 - \exp[-(\epsilon_e - \epsilon_v)/kT]\} \sum_{i=1} B_{ai \rightarrow bi-1} \exp(-i\epsilon_v/kT) \qquad (6)$$

To the approximation that $B_{ai \rightarrow bi+1}$ and $B_{ai \rightarrow bi-1}$ can be replaced by the respective constants B_H and B_L and the quantities $\exp[-(\epsilon_e + \epsilon_v)/kT]$ and $\exp[-(\epsilon_e - \epsilon_v)/kT]$ are zero, the absorbance ratio becomes

$$\frac{A_H}{A_L} = \frac{\nu_H B_H}{\nu_L B_L} \exp(+\epsilon_v/kT) \qquad (7)$$

In order for eq. 7 to agree with the measured absorbance ratio at room temperature, B_L must be greater than B_H by a factor of about 1.4. Figure 8 gives the comparison of measured and calculated absorbance ratios at different temperatures. Up to about 500°, the comparison is quite acceptable. It therefore appears that the change in the structure of the peaks near 2000 mμ can be attributed to changes in populations of the vibrational levels and not to a change in species. Since the selection rule for vibrational transition is $\Delta n = \pm 1$, the lower vibronic transition can

---

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

[27] It is assumed for simplicity that $\epsilon_{va} = \epsilon_{vb} = \epsilon_v$ However, the final result, *i.e.*, eq. 7, is the same as if $\epsilon_{va} \neq \epsilon_{vb}$.

only take place from an excited vibrational level in the ground electronic state. Therefore, at very low temperatures, the peak at 2019 mμ should entirely disappear, a phenomenon which Satten, *et al.*, have observed.

Near the melting point, there appears to be sufficient perturbation to change the transition probabilities in favor of low energy transitions.

The spectrum shown in Fig. 2a appears to indicate some asymmetry in the UCl_6^{-2} ion, probably caused by polarization effects of the cation. Such asymmetry would relax the forbiddance of the pure electronic transitions. This seems to be borne out, among other places, in the structure of the 2000 mμ peak. In this case, the center peak, which must be due to the pure electronic transition, is more intense than those on either side, which appear as shoulders.

Solubility of U(IV) in KCl–AlCl$_3$ Solvents.—Figure 9 summarizes the effect of temperature on the solubility of U(IV) for two different KCl–AlCl$_3$ solvents. These data were obtained spectrophotometrically using solutions which were saturated at the lower temperatures. Extrapolation of the temperature dependence of peaks from high temperatures, where the solution was unsaturated, to lower temperatures allowed the percentage of total uranium in solution to be calculated. The dependence of the solubility of U(III) on the KCl/AlCl$_3$ ratio also follows this trend. The marked increase at KCl/AlCl$_3$ = 1 is indicative that solubility is enhanced by the formation of chloride complexes.

Conclusions

Unfortunately, only one of the species found in these systems has been established with certainty. Until spectra have been correlated with X-ray structural studies, the other species cannot be unambiguously identified. However, data so far obtained are consistent with the postulate that $UCl_x^{(x-4)-}$ and UCl_6^{-2} exist in solutions containing no $AlCl_3$. Another species, possibly UCl_4, exists in $ZnCl_2$, and $U(AlCl_4)_x^{(x-4)-}$ appears to be present in solutions containing an excess of $AlCl_3$. From this, the essential conclusion is that the complexing tendency of U(IV) in the various solvents varies markedly, a condition which prohibits the indiscriminate extrapolation of thermodynamic data from one system to another.

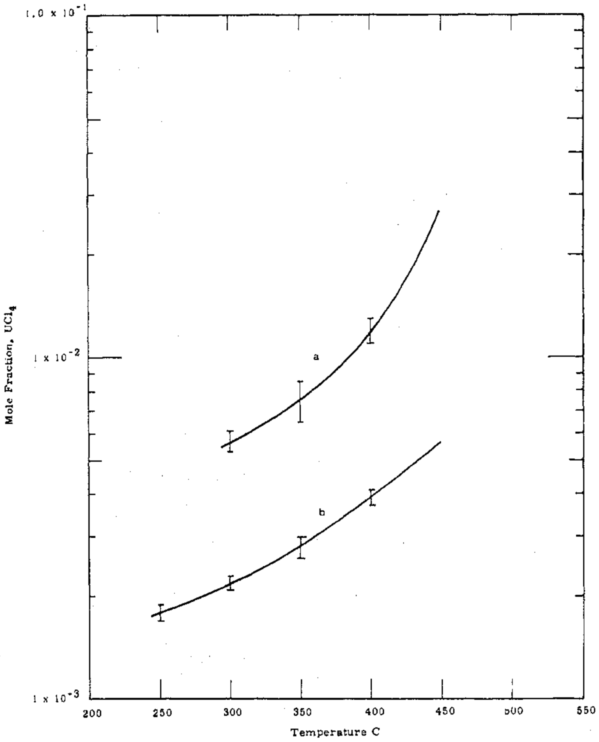

Fig. 9.—The solubility of UCl_4 in KCl–AlCl$_3$: (a) KCl/AlCl$_3$ = 1.03; (b) KCl/AlCl$_3$ = 0.80; mole fraction based on KCl, $AlCl_3$, and UCl_4 as components.

The results so far obtained are in accord with the prediction that the degree of complexation of a solute ion will be dependent on the complexing tendency of the solvent. In the case of pure solvents, this tendency apparently can be related by the charge-to-surface ratio of the solvent cation. Thus, as charge-to-surface ratio decreases, the activity of the anion increases, thereby allowing the solute to complex. Nevertheless, whenever large anions such as $AlCl_4^-$ are present, the effect of the solvent cation is diminished. Hence, the order of complexation of U(IV) becomes

$$CsCl\text{–}CsAlCl_4 = KCl\text{–}KAlCl_4 > CsCl > KCl > NaCl > ZnCl_2$$

Acknowledgments.—The author wishes to acknowledge his indebtedness to Dr. W. E. Keder for supplying the spectrum of $[(C_8H_{17})_3NH]_2UCl_6$ and for his general interest in the problem.