

93. *Magnetochemistry of the Heaviest Elements. Part III.*
The Halides of Ter- and Quadri-valent Uranium.

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Uranium tetrafluoride, tetrachloride, and tetrabromide obey the Weiss-Curie law over the temperature range 77—550° K. The values obtained for the magnetic moment of the quadrivalent uranium ion indicate that in these compounds the ion has a $5f^2$ electron configuration. Uranium trichloride, tribromide, and tri-iodide deviate from the Weiss-Curie law below about 350° K. and are anti-ferromagnetic; the results are interpreted as arising from a $5f^2.6d^1$ electron configuration for the tribromide and tri-iodide, but the electron assignment is not conclusive for the trichloride.

A STUDY of the magnetic properties of compounds of the elements beyond actinium should provide a useful approach to the elucidation of the most stable electronic states of their respective ions. Results previously reported on quadrivalent uranium compounds are rather scattered and occasionally contradictory. For instance, Hutchinson and Elliott (*J. Chem. Physics*, 1948, **16**, 920) report the moments of the hydrated sulphate, hydrated oxalate, and the acetylacetonate complex as 3.52, 3.75, and 3.39 Bohr magnetons, respectively, the electronic ground state being a $5f^2$ configuration. On the other hand, Lawrence (*J. Amer. Chem. Soc.*, 1934, **56**, 776) found a moment of 2.95 for the sulphate and 2.97 for the anhydrous chloride. Measurements on the latter compound by Bommer (*Z. anorg. Chem.*, 1941, **247**, 249) gave a moment of 2.7 Bohr magnetons and were interpreted as being indicative of a $6d^2$ electron configuration. Elliott has reported that uranium tetrafluoride has a moment of 3.30 and that the value is very close to this in a series of double fluorides (*Physical Rev.*, 1949, **76**, 431). In uranium dioxide U(IV) has an effective moment of 3.20 (Part II, Dawson and Lister, *J.*, 1950, 2181). Few measurements have been reported on U(III) compounds: Lawrence (*loc. cit.*) found that the chloride and the sulphate had moments of 3.22 and 3.17 magnetons, respectively. In order to obtain a more complete set of data, the author has investigated the susceptibility-temperature relations of UF₄, UCl₄, UBr₄ and of UCl₃, UBr₃, and UI₃.

EXPERIMENTAL.

The measurements were made on the balance described in Part I (*J.*, 1950, 2177), the samples being enclosed in sealed capillary tubes under an atmosphere of dry nitrogen. The order of measurements on each sample was: room temperature, low temperatures, high temperatures, room temperature; by this means a check was made against decomposition of the sample at high temperatures. A second sample from a separate preparation was taken over the same range of temperatures and good agreement

Uranium tetrafluoride.			Uranium tetrachloride.			Uranium tetrabromide.		
T, °K.	10 ⁶ χ, g.	10 ⁶ χ per U(IV).	T, °K.	10 ⁶ χ, g.	10 ⁶ χ per U(IV).	T, °K.	10 ⁶ χ, g.	10 ⁶ χ per U(IV).
77	21.82	6912	90	23.41	8919	77	19.27	10,930
90	20.62	6536	196	13.30	5177	90	17.30	9,828
198	13.20	4206	294	9.68	3802	197	9.15	5,281
295	10.10	3232	333	8.64	3406	293	6.33	3,709
334.5	9.04	2900	372	7.87	3114	359	5.21	3,083
416	7.80	2510	388	7.56	2996	383.5	4.87	2,894
500	6.72	2171	413	7.09	2818	418.5	4.49	2,680
			441	6.74	2684	455	4.15	2,491
			551	5.89	2363	513	3.68	2,229
						569	3.32	2,032

Uranium trichloride.			Uranium tribromide.			Uranium tri-iodide.		
T, °K.	10 ⁶ χ, g.	10 ⁶ χ per U(III).	T, °K.	10 ⁶ χ, g.	10 ⁶ χ per U(III).	T, °K.	10 ⁶ χ, g.	10 ⁶ χ per U(III).
90	25.97	8952	90	23.95	11,600	77	21.50	13,520
198	14.78	5095	198	14.32	7,005	90	19.59	12,340
300	10.03	3456	294	9.91	4,896	197	10.60	6,779
367	8.41	2899	342	8.54	4,243	293	7.20	4,673
395	7.86	2709	368	7.91	3,942	337	6.29	4,111
426	7.34	2530	394	7.38	3,687	352	6.02	3,943
456	6.88	2372	439	6.48	3,256	365	5.76	3,784
490	6.35	2189	457	6.19	3,119	394	5.32	3,509
509	6.18	2130	483	5.83	3,949			

was obtained in each case. Reproducible results on the tri-iodide were found to be possible only on freshly prepared material, and no agreement was obtained between several samples of the tetraiodide, which is therefore omitted from this discussion.

The UCl_3 , UI_3 , and UBr_4 were prepared directly from samples of the same batch of uranium metal turnings in a graded furnace according to the methods of Gregory (Manhattan District Declassified Document, 1755). A spectrographic analysis of the UI_3 gave $<0.01\%$ by weight of iron, chromium, nickel, cobalt, and manganese combined. Uranium tribromide was formed by hydrogen-reduction of the tetrabromide. Uranium tetrachloride was prepared by reaction of the iron-free oxide with carbon tetrachloride, followed by sublimation of the product *in vacuo*. The tetrafluoride was a good commercial grade.

The results are given in the table, the figures in the third column for each compound being obtained after correction for the diamagnetism of the anions and the cations. These values were calculated by Angus's method (*Proc. Roy. Soc.*, 1932, *A*, **136**, 569) and were $\text{F}^- = -7.25 \times 10^{-6}$, $\text{Cl}^- = -22.9 \times 10^{-6}$, $\text{Br}^- = -36.65 \times 10^{-6}$, $\text{I}^- = -55.3 \times 10^{-6}$, $\text{U(IV)} = -31.5 \times 10^{-6}$, $\text{U(III)} = -53.3 \times 10^{-6}$. The values for the uranium ions are calculated by using an electron configuration of $5f^2$ for U(IV) and $5f^3 \cdot 6d^1$ for U(III) .

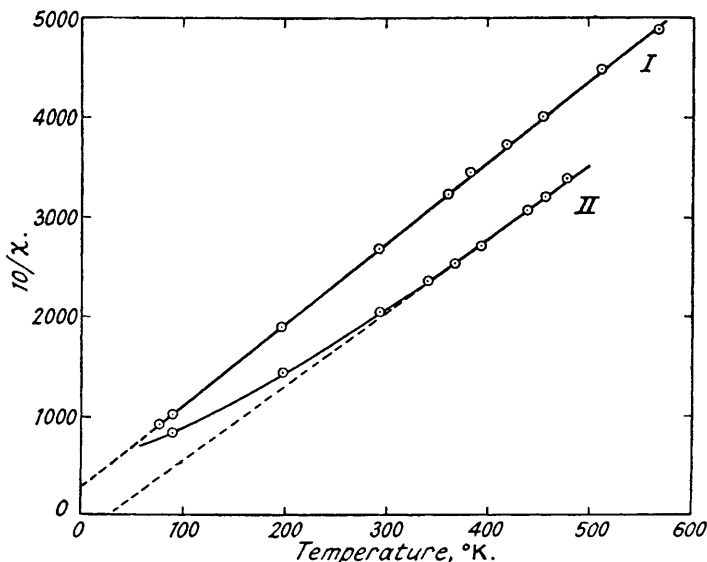
DISCUSSION.

The Weiss constants and the magnetic moments calculated by the Weiss-Curie law from the data in the above table are given below. The tetrahalides follow the Weiss-Curie law over the temperature range studied, but the trihalides show marked deviations at lower tem-

Compound.	UF_4 .	UCl_4 .	UBr_4 .	UCl_3 .	UBr_3 .	UI_3 .
Δ	-116°	-62°	-35°	-29°	$+25^\circ$	$+5^\circ$
μ per U ion	3.28	3.29	3.12	3.03	3.29	3.31

peratures and the moments quoted are those obtained in the higher temperature region. The susceptibility-temperature behaviour of the two groups of compounds is compared in the figure.

In the case of the tetrahalides the variation of Δ from fluoride to bromide is such as may be



I. Reciprocal susceptibility-temperature curve for the U(IV) ion in UBr_4 .
 II. Reciprocal susceptibility-temperature curve for the U(III) ion in UBr_3 .

expected from the trend of molar volumes, and most of the change in Δ would seem to arise from Heisenberg exchange interaction rather than variation in the crystalline field splitting. The measured magnetic moments for U(IV) can be explained on the assumption of a $5f^2$ electron configuration with the exchange effect and the crystalline field splitting reducing the effective moment below the theoretical value of 3.58 Bohr magnetons for Russell-Saunders coupling. The calculated value for $j-j$ coupling is 3.83, and the same conclusions would still apply.

Although there is a greater amount of covalent nature in the tetrabromide than in the

tetrafluoride, in view of the comparative constancy of the effective moment the orbitals concerned do not seem to involve $5f$ hybrids.

The situation is rather different for the trivalent compounds, however. The appearance of a positive Δ value in the bromide and iodide, together with deviations from the Weiss-Curie law, indicate that the electron additional to those in the U(IV) ion is of a different species. The situation is comparable with that in the transition elements (*e.g.*, Klemm and Grimm, *Z. anorg. Chem.*, 1942, **249**, 209) and is indicative of the strong parallel coupling of adjacent spin vectors to be expected for unshielded outer electrons. The trichloride shows a less intense coupling, but still deviates from the Weiss-Curie law at low temperatures. The "spin-only" value of the effective moment for three electrons is 3.87 Bohr magnetons. The lowest-lying energy levels predicted by Hund's rule for Russell-Saunders coupling are $4I_{9/2}$ ($\mu_{\text{eff.}} = 3.62$) and $4K_{11/2}$ ($\mu_{\text{eff.}} = 4.60$) for $5f^3$ and $5f^2.6d^1$ configurations, respectively; $j-j$ coupling gives effective moments a little higher than the L-S coupling, and a further low-lying state for the $5f^2.6d^1$ configuration is $4H_{7/2}$ ($\mu_{\text{eff.}} = 2.65$), corresponding to complete orbital quenching of the $6d$ electron. In view of the various types of coupling and quenching theoretically possible in this case, it is difficult to deduce an unambiguous electron configuration by comparison of the observed and calculated moments, but the observed value of about 3.3 magnetons is not inconsistent with a $5f^2.6d^1$ configuration in which the orbital contribution of the $6d$ electron is quenched together with partial quenching of the $5f$ electrons, and in which there is strong spin coupling between adjacent $6d$ electrons. This spin coupling would not have been expected by comparison with the $5f^3$ configuration of the U(IV) ion and does not occur in the corresponding rare-earth ion. Consequently, the magnetic data are interpreted as arising from electrons in a $5f^2.6d^1$ configuration in the tribromide and tri-iodide. The coupling is not so great in the trichloride and it is not possible on these results definitely to assign the third electron to either the $5f$ or the $6d$ level.

A preliminary experiment on the effect of dilution of uranium tribromide with isomorphous lanthanum bromide shows that at 90% dilution the susceptibility of the U(III) ion follows the Weiss-Curie law much more closely and the moment rises higher than 4.6 magnetons, but there remains a rather high Δ value which presumably arises from the crystalline field effect.

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