The Critical Ionization Potentials of Uranium Hexafluoride and Hydrogen Fluoride

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THE critical ionization potentials of uranium hexofluoride and of hydrogen fluoride were determined by using a VG1A ion gauge. The filament emission was held constant at such a value that the grid current was in a plateau region. The grid-to-filament potential was then varied and the onset of ionization determined by plotting the ion current as a function of the applied voltage. The ions were collected on the plate by application of a small fixed potential. The effects of secondary emission and space charge were evaluated by measuring the ionization potential of mercury. The correction was determined, using the value of 10.4[1] volts for the first ionization potential of mercury, and was subtracted from the potential observed for uranium hexafluoride. Measurements were made with hydrogen fluoride to eliminate the possibility that the potential observed with uranium hexafluoride was due to hydrolysis products. The measurements upon uranium hexafluoride were repeated in a 60° mass spectrometer of the Nier type so that ions other than the UF_5^+ could be identified and measured. The ionizing case and the electron trap were operated at the same potential so that the voltage drop from the filament to these elements was a measure of the ionization potential. The effect of space charge, thermal excitation, and secondary emission in the ionizing region were evaluated by using mercury as reference gas. The filament emission was held constant at 1.4 ma and no potentials except that between filament and ionizing case were varied after measurements upon mercury. The potentials were measured with a voltmeter which had been calibrated carefully against a laboratory potentiometer. The critical potential was determined by the intersection of the plots of ion current against voltage before and after reaching the critical potential. The mean value for several determinations upon the mercury standard was 15.1 volts. A correction of −4.7 volts was accordingly applied to the observed critical ionization potentials for the individual uranium fluoride ions. The critical ionization potentials are shown in Table I. These data

TABLE I. Critical ionization potentials of U, UF, and HF.

Ion	Critical ionization potential (ev) Spectrometer	Triode
UF_5^+	15.5	15.9
UF_4^+	20.1	—
UF_3^+	23.5	—
UF_2^+	29.9	—
UF_1^+	37.9	—
U^+	50.3	—
HF	—	5.4

may be regarded as giving a correct representation of the order of magnitude, but a probable error range of from 5 percent for the UF_5^+ ion to 15 percent for the U^+ appears likely because of the wide departure of the potentials from that of the reference gas.

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[1] W. Bleakney, Phys. Rev. **35**, 139 (1930).

A Note on the Spectrum of Th III

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THE second spark spectrum of thorium has been photographed on the three-meter vacuum spectrograph from 2000A to 350A, using a vacuum spark source between metallic electrodes which is known to excite the III and IV spectra most intensely. As a further aid in distinguishing the lines of Th III, the same electrodes were used in an atmosphere of nitrogen at a lowered potential. The strong lines of Th IV are easily spotted for the most part, but the measurement of their wave-lengths leaves something to be desired in the way of accuracy.

The lines of Th III, which are the subject of this note, are very numerous especially in the region between 600A and 350A. These short lines in higher orders occur throughout

TABLE I.

First system Even terms	Second system Even terms	Second system Odd terms
201361 ($j=3$ or 4)	221728 ($j=2$)	105474.8 ($7p7s$) $^3P_2$
69708.7 ($j=3$)	224520 ($j=2$)	107722.6 ($j=2$ or 3)
64713.6 ($j=3$)	265075 ($j=1$)	107875.9 ($j=2$)
	69419.5 ($j=5$)	108841.0 ($j=1$ or 2)
		118756.1 ($j=2$) (uncertain)
		116475.4 ($j=2$)
		120168.4 ($j=2$ or 3)

the spectrum up to the fifth and even the sixth order. An attempt has been made to employ them to tie the whoel spectrum together, so as to obtain consistent accuracy below 2000A.

The spectrum of Th III has been partially analyzed into two systems of terms[1] without any intercombinations between them. The author has sought these intercombination lines in the vacuum region without any certain success. A factor which gives a promising number of possible intercombination lines has the value 12328 cm^{-1} to be added to the term values of the second system, so that based upon $5f6d\ ^3H_4$ as zero, the value of $6d7s\ ^1D_2$ would be 69328. I am informed privately by Dr. Klinkenberg that there are theoretical objections to a factor of such numerical size in the general structure of the III spectrum and its relation to the II spectrum.

In the work so far, a number of terms have been found which constitute an extension of Th III into the Schumann region. These, together with their j values, are shown in Table I.

[1] T. L. De Bruin, P. F. A. Klinkenberg, and P. Shuurmans, Zeits. f. Physik **118**, 58 (1941).