

where  $a$  is the average displacement of a surface atom from its position of equilibrium. This assumption may be avoided, and the same results obtained, provided

$$a \ll \lambda$$

where  $\lambda$  is the wave-length of the gas atom.

Both conditions are satisfied with helium and tungsten.

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### The Ultimate Lines of Element 87

In a communication to the Physical Review the writer presented an estimate of the wave-lengths of those lines which may be expected to appear when a sample containing traces of the element of atomic number 87 is examined spectroscopically.<sup>1</sup> The numerical value of each line is dependent on the quantum defects of two levels, and as an error of  $\pm 0.005$  in the estimation of the latter produces an uncertainty of about  $\mp 180\nu$  in the term value, the wave-lengths can be off by as much as 200A should the errors in the estimation of the levels be of opposite sign. It is therefore desirable to form an independent estimate of the wave-lengths of the first two doublets in the principal series spectrum of ekacaesium by a method which involves one, instead of two extrapolations, and for which data are available to test its reliability in constructing the known spectrum of radium.

TABLE I. *Spectrum of singly ionized radium.*

$N_a$	$\lambda_a$	$N_b$	$\lambda_b$	$\lambda_a/\lambda_b$
$1^2S-2^2P_2: \lambda_a/\lambda_b=0.006139N_a+1.7799$				
38	4077.714	30	2025.5	2.01319
56	4554.037	48	2144.39	2.12370
88	3814.44 (3828)	80	1649.8	2.31206 (2.3201)
$1^2S-2^2P_1: \lambda_a/\lambda_b=0.007439N_a+1.7618$				
Sr	4215.515	Zn	2061.9	2.04448
Ba	4934.09	Cd	2265.03	2.17838
Ra	4682.20 (4693)	Hg	1942.3	2.41065 (2.4164)

A method of extrapolation which fulfills these requirements assumes a linear relationship between the atomic number ( $N$ ) and the ratio ( $\lambda_a/\lambda_b$ ) of the wave-lengths of corresponding lines belonging to the spectrum of elements of sub-groups  $a$  and  $b$  with total quantum numbers  $n+1$  and  $n$  respectively. Thus, in the second periodic group of elements the ratio of the wave-lengths of the *raies*

<sup>1</sup> H. Yagoda, Phys. Rev. **38**, 2298 (1931).

*ultimes* emitted by strontium and zinc, barium and cadmium, and radium and mercury are proportional to the atomic numbers of either sub-group of elements. Table I shows that the wave-lengths of the radium lines can be closely approximated by this method, the estimates being 3828A and 4693A, whereas the observed lines of the doublet reside at 3814.44A and 4682.20A. Again, the difference between the wave-numbers of the two lines is 4818 $\nu$  which compares favorably with the measured doublet separation of 4857.2 $\nu$ .

TABLE II. *Red lines of neutral ekacaesium.*

$N_a$	$\lambda_a$	$N_b$	$\lambda_b$	$\lambda_a/\lambda_b$
$1^2S-2^2P_2: \lambda_a/\lambda_b=0.010860N_a+2.0001$				
37	7800.30	29	3247.548	2.40190
55	8521.15	47	3280.67	2.59738
87	(7150)	79	2427.96	(2.9449)
$1^2S-2^2P_1: \lambda_a/\lambda_b=0.012014N_a+1.9830$				
Rb	7947.63	Cu	3273.964	2.42753
Cs	8943.6	Ag	3382.89	2.64378
87	(8104)	Au	2675.95	(3.0282)

TABLE III. *Violet lines of neutral ekacaesium.*

$N_a$	$\lambda_a$	$N_b$	$\lambda_b$	$\lambda_a/\lambda_b$
$1^2S-3^2P_2: \lambda_a/\lambda_b=0.007464N_a+1.7994$				
37	4201.81	29	2024.33*	2.07557
55	4555.3	47	2061.19*	2.20992
87	(4225)	79	1725.5†	(2.4488)
$1^2S-3^2P_1: \lambda_a/\lambda_b=0.007668N_a+1.7973$				
Rb	4215.58	Cu	2025.67*	2.08097
Cs	4593.2	Ag	2069.85*	2.21899
87	(4328)	Au	1756.0†	(2.4644)

\* A. Fowler, "Report on Series in Line Spectra," p. 111 (1922) London.

† W. M. Hicks, Phil. Mag. (6) **38**, 26 (1919).

A similar set of operations on the members of group I may be expected to yield equally reliable results in the estimation of the corresponding lines of element 87. These calculations are presented in Tables II and III;

quantities in parentheses indicating extrapolated values. Unless otherwise noted the wave-lengths are those given in the International Critical Tables.<sup>2</sup> A comparison of the new estimates with the values secured from the quantum defect relationship (Table IV) shows that only in the case of the  $1^2S-2^2P_2$

TABLE IV. *Ultimate lines of element 87.*

Method	Red doublet		Violet doublet	
	$1^2S-2^2P_2$	$1^2S-2^2P_1$	$1^2S-3^2P_2$	$1^2S-3^2P_1$
Quantum defects	7460	8130	4260	4310
Sub-group ratios	7150	8104	4225	4328

line of the red doublet do the two methods yield markedly different results. The doublet separations of  $1646\nu$  in the red, and  $558\nu$  in the violet region are in good agreement with independent estimates for these intervals, the mean of which are  $1690 \pm 100\nu$  and  $550 \pm 50\nu$ .<sup>3</sup>

#### Absorption of Oxygen in the Region of Short Wave-lengths

The dispersion of oxygen between the visible and 1900A can be described quantitatively<sup>1</sup> by two resonance wave-lengths  $\lambda_1 = 1469\text{A}$  and  $\lambda_2 = 544\text{A}$  with the corresponding number of oscillators  $f_1 = 0.20$  and  $f_2 = 5.93$ .

In order to study the physical significance of this result we have investigated the absorption of oxygen down to 300A by means both of a small fluorite and a large grating spectrograph. The latter, designed by Compton and Boyce,<sup>2</sup> was used for qualitative measurements only. Flowing oxygen was introduced into the spectrograph at pressures between 0.25 and 0.002 mm. Besides the oxygen, only some helium, at about 0.001 mm pressure, coming from the light source, was in the spectrograph. The light source was an uncondensed capillary discharge at 0.1 mm pressure in helium containing perhaps one percent of impurities. This gave emission lines distributed over the whole of the spectral range investigated. The conspicuous impurities were oxygen, hydrogen and nitrogen.

<sup>1</sup> R. Ladenburg and G. Wolfsohn, *Phys. Rev.* **40**, 123 (1932).

<sup>2</sup> K. T. Compton and J. C. Boyce, *Phys. Rev.* **40**, 1038 (1932).

Judging from the nature of the agreement between the calculated and observed spectral lines in the case of the radium spectrum, it may be concluded that in the spectrophotographic examination of mineral concentrates lines in the region of  $4225 \pm 15\text{A}$  and  $4328 \pm 15\text{A}$  will be observed should the sample contain ekacaesium. The investigation also indicates that the first doublet of the principal series will appear in a region that is better adopted for its visual observation than has been supposed by previous workers.<sup>4</sup>

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<sup>2</sup> *Inter. Critical Tables* **5**, 323 (1929).

<sup>3</sup> Detailed calculations will be published in the July or a later issue of the *Journal of the American Chemical Society*.

<sup>4</sup> K. T. Bainbridge, *Phys. Rev.* **34**, 752 (1929); J. Papish and E. Wainer, *J. Am. Chem. Soc.* **53**, 3818 (1931); W. F. Meggers, *Science Supplement* **74**, No. 1926, 10 (1931)

The results confirm some of the earlier experiments of Lyman, Leifson and Hopfield. There are two strong absorption regions in oxygen, one between 1750 and 1300, with a maximum in the neighborhood of 1400A, and another below 1100A and still quite strong at 300A, separated by a gap which is transparent for a 4 meter path of pure O<sub>2</sub> at 0.25 mm pressure. As nitrogen proved to be also transparent in this region, it seems hopeful to use wave-lengths between 1300 and 1100A for photochemical reactions, the light source and the reaction chamber being separated by CaF<sub>2</sub> or LiF windows and a few millimeters of air. Such a light source is under construction.

The two resonance wave-lengths calculated from the dispersion measurements correspond obviously to the two observed absorption regions. Their positions are in fair agreement with the estimated centers of gravity of the absorption bands.

For quantitative measurements we used a fluorite spectrograph, like one constructed by Cario and Schmidt-Ott,<sup>3</sup> the hydrogen spectrum of a capillary tube as light source and

<sup>3</sup> G. Cario and H. D. Schmidt-Ott, *Zeits. f. Physik* **69**, 719 (1931).