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COLLEGE OF NEW YORK UNIVERSITY]

AN ESTIMATION OF SOME SPECTRAL PROPERTIES OF ELEMENT 87

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Evidence for the existence of minute quantities of element 87 in several alkali-bearing minerals has recently been secured by Allison and his collaborators¹ using the magneto-optic method of analysis, and also by Papish and Wainer² through x-ray analysis of a concentrate from the mineral samarskite. The latter investigators have questioned the evidence adduced from the magneto-optic analyses, claiming that the minima attributed to the missing alkali element are also given by certain complex ions, as SnCl_3^+ and ReCl^+ . More refined measurements of the position of the minima by McGhee and Lawrenz³ and by Allison and his collaborators⁴ reveal that a conflict between the points used to identify element 87 and those given by the complex ions is not probable.

The delicacy of spectroscopic analysis is well known, and the fact that two homologs of element 87, rubidium and cesium, were first discovered in that way by R. Bunsen and G. Kirchhoff suggests that the spectroscopic method of analysis may also prove useful in establishing the existence of the element in question. The several investigators^{2,5} who have approached this problem placed little weight on the negative results obtained from their spectroscopic analyses, claiming that the spectral lines of the principal series are located in the far-red end of the spectrum where visual and photographic sensitivity are very poor. It is true that by extrapolating a wave length-atomic number function through potassium, rubidium and cesium, a value for the first transition is obtained that locates the line in the red end of the spectrum, but such an extrapolation, as will soon be shown, is not justified. Furthermore, in the practical detection of traces of potassium, rubidium and cesium, the second transition of the series is used for the identification of the element, as the respective lines reside in the violet region of the spectrum where photographic sensitivity is close to its maximum value.

The present writer has shown that the $1^2\text{S}-3^2\text{P}_2$ transition has an approximate wave length of 4260 Å. This value was obtained through the use of an empirical observation that the quantum defect of a given elec-

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¹ Allison and Murphy, *Phys. Rev.*, **35**, 285 (1930).

² Papish and Wainer, *THIS JOURNAL*, **53**, 3818 (1931).

³ McGhee and Lawrenz, *ibid.*, **54**, 405 (1932).

⁴ Allison, Bishop, Sommer and Christensen, *ibid.*, **54**, 613 (1932).

⁵ Meggers, *Science Supplement*, **74**, 10 (1931).

tronic level (Q) in a sequence of homologous elements is approximately a linear function of the total quantum number (n) of the valence electron.⁶ Data are lacking by which this figure can be directly compared, but its validity can be partially tested by the ionization potential predicted by the same method, as the latter can be calculated from several independent considerations.

It is generally known that in the periodic classification of the elements the properties of the members of the second and fourth periods exhibit anomalous behavior when the properties of a given group of elements are considered. The question arises whether members in the seventh period, and element 87 in particular, are also exceptions to the rule governing the properties of the group. The writer has been interested in this problem for some time, as it is of practical importance in developing a method for the concentration of the missing element.⁷ The chief evidence available for the solution of this problem resides in the measurements of the optical spectrum of radium and its analysis into terms by Hicks.⁸ When the spectral properties of RaII are compared with those of the other alkaline earths, it is observed that the wave lengths of the first two transitions are anomalous with respect to the similar lines of calcium, strontium and barium, and that both the ionization potential and the doublet separation of the first transition exhibit marked departures from the relations connecting the respective properties of the other alkaline earth elements. Such an exceptional behavior might be expected from the intrusion of the rare-earth elements in the sixth period. In formulating a relationship between the ionic potential and the ionization potential, Cartledge⁹ has shown that for ions of only slightly larger size than cesium and barium, unusual behaviors can be expected owing to the great polarizing effect of the valence electron upon the ion. It is highly probable that the spectroscopic properties of element 87 will not follow the same trend as the triad, potassium, rubidium and cesium, and that any theoretical or empirical method which permits the correct prediction of the known properties of the singly ionized radium atom may also furnish a correct guide to the unknown properties of the neutral eka-cesium atom.

Table I represents a summary of the different methods employed in the estimation of the probable ionization potential of element 87. The first value was calculated from deductions made by Fermi¹⁰ concerning the

⁶ Yagoda, *Phys. Rev.*, **38**, 2298 (1931).

⁷ "Investigation of a Pollucite Ore for the Detection of Eka-cesium," H. Yagoda, dissertation at New York University (June, 1931). I wish to take the opportunity here, of expressing my indebtedness to Prof. H. M. Partridge for suggesting this problem to me.

⁸ "International Critical Tables," Vol. V, 1929, p. 392; W. M. Hicks, "Analysis of Spectra," Cambridge, 1922, p. 276.

⁹ G. H. Cartledge, *THIS JOURNAL*, **52**, 3076 (1930).

¹⁰ Fermi, *Z. Physik*, **49**, 550 (1928).

quantum defects of the S levels of the elements as a function of their atomic number (N). Since Q is known, the value of the normal term can be calculated from the relationship

$$\nu = RZ_0^2/(n - Q)^2$$

where ν represents the wave number of the level, R the Rydberg constant and Z_0 the mean effective nuclear charge for the outer portion of the electronic orbit. For the element in question, $\nu = (109,680 \times 1^2)/(7 - 5.22)^2 = 34,600$, and the ionization potential, $V = \nu/8106 = 4.27$ volts.

Cartledge⁹ has shown that V can be calculated from the ionic potential (ϕ); this leads to a value of 4.55 volts. In a private communication Cartledge states: "This extrapolation value is in error, both on account of the disturbances introduced by the abnormally great polarizability of the seventh-period ions, and because of the uncertainty of the radius of the Ra^{++} ion."¹¹ From the several estimates of the radius, Cartledge finds that a probable value of the ionization potential resides between 4.2 and 4.4 volts.

The ratio of corresponding alkali and alkaline earth terms is nearly a constant for all the family members. The logarithm of this ratio plotted against n gives a smooth curve which can be extrapolated for the particular value of Eka-CsI/RaII with a fair degree of accuracy; for the 1^2S term this ratio is equal to 0.399. The value of 4.05 volts published by Bainbridge¹² was probably obtained by a similar calculation.

Hume-Rothery¹³ has recently demonstrated from considerations of the interatomic distance between atoms in metallic crystals that n^2V is a linear

TABLE I
IONIZATION POTENTIAL AND 1^2S TERM OF ELEMENT 87

Method	V	1^2S in ν	Quantity directly estimated
Statistical mechanics ¹⁰	4.27	34,600	Q from N
Ionic potentials	4.3	34,900	ϕ from Ra^{++} data
Ratio Eka-CsI/RaII levels	4.09	33,100	Log of term ratios
Quantum defect rule	4.06	32,900	Q from n
Isoelectronic of radium ¹²	4.05	32,800	
$n^2V = aN^{2/3} + b$	3.89	31,500	V from N and n
Atomic volume relationships	3.77	30,600	V from ν and n
Probability numbers ¹⁴	3.58	29,010	1^2S from N
Weighed average	4.11	33,320	Last two values excluded

function of $N^{2/3}$. On testing this relationship, the writer has found that for the neutral alkali atoms n^2V actually varied with the 0.6664 power of

¹¹ Cartledge, *THIS JOURNAL*, **50**, 2855 (1928).

¹² Bainbridge, *Phys. Rev.*, **34**, 752 (1929).

¹³ Hume-Rothery, *Phil. Mag.*, [7] **11**, 670 (1931); [7] **13**, 196 (1932); Yagoda, *ibid.*, [7] **13**, 1163 (1932).

¹⁴ Loring, *Chem. News*, **140**, 178, 202, 242 (1930); **143**, 18, 98, 149 (1931).

N , which is in very good agreement with the theoretic deduction, but that for the singly ionized atoms of the alkaline earth elements much better agreement with the observed data is obtained by using the relationship

$$\log n^2V = 0.6188 \log N + 1.4667$$

In both families, however, the first members, lithium and beryllium, show marked departures from these relationships, and when the above equation is extrapolated for V of RaII a value of 9.53 volts is obtained, whereas the constant calculated from the spectrum of the element is equal to 10.32 volts. The value of 3.89 volts estimated for element 87 from the relationship

$$n^2V = 9.836 N^{2/3} - 2.580$$

is probably also too low.

The atomic volume of eka-caesium can be estimated from the observation made by Hicks¹⁵ that in the alkali family the atomic volume (v) is expressed by the product of a constant k , and an integer s characteristic of the element. At 20°, $v = 11.5 \times 7 = 80.5$ cc. For the alkalis, the present writer has found that the ionization potential is connected with the atomic volume by the relationship $Vv^{1/4} = K$, where K is equal to 11.3 at 20°. These relationships indicate that the ionization potential of the element is 3.77 volts. However, lithium is a marked exception to both generalizations, hence the validity of the estimates for v and V for eka-caesium is also questionable. The lowest value of the ionization potential is that published by Loring;¹⁴ this was secured by extrapolation of the 1²S levels through all the alkalis.

In the alkaline earth spectra V diminishes progressively from beryllium to barium, but the value for radium is anomalous, being greater than that of barium. Therefore, the ionization potential of eka-caesium will probably also be greater than that of caesium. Of the values calculated, those numerically less than 3.88 volts (which is the ionization potential of caesium) have but little significance. The average of the estimates above 3.88 volts is 4.11 ± 0.2 volts. The particular value of V calculated from the quantum defect rule, 4.06 volts, is in good agreement with the average value.

Doublet Separations.—Each transition of the principal series spectra of the alkali atoms consists of two members of which the line of shorter wave length is the more intense, and in which the distance between the lines increases progressively from lithium to caesium. The separation of the lines in the first and second doublets is an important criterion in the spectro-

¹⁵ Hicks, *Proc. Roy. Soc. (London)*, **83**, 226 (1910). Recently, W. Biltz has shown that the atomic volumes of the elements at the absolute zero (v_0) are expressed by the relationship, $v_0 = 11.3 n/Z_0$, where Z_0 is the periodic group number of the element. In many cases Hicks' integers (s) are identical to n ; *Z. physik. Chem.*, Bodenstein Festband, 198 (1931); also, W. Biltz and K. Meisel, *Z. anorg. Chem.*, **198**, 191 (1931).

scopic identification of the alkali element in question. Bell¹⁶ has demonstrated that for the known alkali atoms the doublet separations are expressed by the following equations:

$$2^2P_j: \log \Delta\nu = 2.1515 \log N - 0.9997; \text{ when } N = 87, \Delta\nu = 1490$$

$$3^2P_j: \log \Delta\nu = 2.160 \log N - 1.500; \text{ when } N = 87, \Delta\nu = 490$$

In view of the unusual relationships existent in the seventh period, I have thought it desirable to test similar equations on the alkaline earth family in order to judge how well they predicted the doublet separations of the singly ionized radium spectrum.

$$2^2P_j: \log \Delta\nu = 1.925 \log N - 0.134; \text{ when } N = 88, \Delta\nu = 4040$$

$$3^2P_j: \text{ data are available only for the BeII and MgII spectra}$$

The observed doublet separation in the case of radium is 4857.2ν . The above expressions, therefore, need modification in order to account for members of the seventh period. When corrective terms are introduced into Bell's expressions, their general precision is lost, but the range of extrapolation is improved.

$$\text{Alkaline earth II spectra, } 2^2P_j: \log \Delta\nu = 1.537 \log (N - n^2) + 1.228; \text{ when } N = 88 \\ \Delta\nu = 4710$$

$$\text{Alkali I spectra, } 2^2P_j: \log \Delta\nu = 1.543 \log (N - n^2) + 0.771; \text{ when } N = 87, \Delta\nu = 1620$$

By extrapolating the ratio of the doublet separations of corresponding alkali and alkaline earth atoms a value of 1660ν is obtained for the 2^2P_j separation of element 87. Bainbridge¹² finds that this value is equal to $1675 \approx 50\nu$. It would seem then, that the separation of the first doublet is in the region of 1650ν .

However, a much larger value is obtained by applying the Landé relationship¹⁷

$$\Delta\nu = \frac{R\alpha^2 Z_0^2 Z_i^2}{(n^*)^3 l(l+1)} \left[1 + \frac{5}{8} (\alpha Z_i)^2 + \frac{53}{128} (\alpha Z_i)^4 + \dots \right]$$

Here α represents the fine structure constant $2\pi e^2/hc$, n^* and l the effective and azimuthal quantum numbers, and Z_i the effective nuclear charge for the inner portion of the electronic orbit. For the first transition of the singly ionized radium spectrum, $Z_i = 83.6$, $n^* = 2.784$, $Z_0 = 2$, $l = 1$ and $\alpha = 0.007284$.¹⁸ These quantities lead to a value of 4860ν , which is in excellent agreement with the observed doublet separation. In order that the Landé formula be applicable to the spectrum of element 87, n^* and Z_i for the 2^2P_2 and 3^2P_2 levels must be known. The mean value of n^* for the 2^2P_2 level is 2.365 .¹⁹ Landé has shown that Z_i differs only by a small

¹⁶ H. Bell, *Phil. Mag.*, [6] **36**, 337 (1918). The coefficients of the following two equations have been reevaluated to fit more recent measurements of the doublet separations.

¹⁷ Landé, *Z. Physik*, **25**, 46 (1924).

¹⁸ Birge, *Phys. Rev. Supplement*, **1**, 1 (1929).

¹⁹ This number was obtained by calculation from the mean of the two estimates available for the 2^2P_2 level of eka-caesium, *viz.*, Bainbridge¹² finds $19,670\nu$, and from the quantum defect rule⁸ $19,540\nu$.

quantity from the atomic number of the atom. The screening constant (σ) is larger for an alkali atom than for the corresponding alkaline earth atom, the ratio of the two being 1.45 for the heavy atoms; also σ for RaII is less than that of BaII. The screening constant for the neutral eka-caesium atom should therefore be smaller than that of the neutral caesium atom, and be about 1.45 times as large as that of the singly ionized radium atom. A value of 6.4 satisfies these conditions; hence $Z_i = 80.6$, and $\Delta\nu$ for 2^2P_2 is equal to 1810ν . Assuming that Z_i for the second doublet is approximately the same as for the first, and that the value of 3^2P_2 is 9416ν ,⁶ then the displacement of the doublet in the violet region, as given by the Landé formula, is 600ν .

Now, the ratio of the displacements of the first and second doublets in the spectra of the neutral alkali atoms is nearly a constant for the group, and in the case of element 87 the ratio is probably 3.07. Dividing the average displacement of the first doublet, as found by the empirical relationships, by this figure gives as the displacement of the second doublet $1650/3.07 = 538\nu$. It can be assumed, then, that the distance between the two lines characterizing the doublet in the violet region is approximately $570 \approx 30\nu$. The average displacement for the first doublet is $1690 \approx 100\nu$.

Of the two lines constituting the doublet, the line of shorter wave length is the more intense. From the sum rule of Burger and Dorgelo²⁰ it may be expected that in the first doublet the major line will be twice as intense as the component of longer wave length; and from the empirical relationship formulated by Sambursky²¹ it may be conjectured that in the second doublet the major line will be 8-9 times more intense than its satellite.

By correlating the limit of spectroscopic detection with the sensitivity of the recording device for the wave length and intensity of the light emitted on the return of electrons from the several energy levels to the alkali ions when the salts are dissociated in a flame at 2000°K ., it can be deduced that about 10^{-5} g. of eka-caesium will be sufficient for the visual observation of the most persistent line in the red end of the spectrum²² and that it will also suffice to record a photographic image of the *raie ultime* in the violet region. Experiments on the spectrophotographic detection of minute traces of potassium, rubidium and caesium in the presence of large amounts of the other elements reveal that the simultaneous

²⁰ Burger and Dorgelo, *Z. Physik*, **23**, 258 (1924).

²¹ Sambursky, *ibid.*, **49**, 731 (1928).

²² The wave length of the most persistent line in the red has been estimated at 7460 \AA .;⁶ Bainbridge¹³ assigns to it a value of 7600 \AA . H. Deslandres, *Compt. rend.*, **191**, 169 (1930), has observed that the constant $d = 1062.5\nu$ enters into the wave number relationships of the *raies ultimes* of the elements. Using a multiple of 13 (selected with the aid of the measured spectrum of radium) for element 87, a value of 7240 \AA . is obtained for this line.

presence of the other ions in the flame does not appreciably affect the photographic sensitivity for the *raies ultimes* of the alkalies, and that, in particular, a thousand-fold concentration of sodium does not interfere with the spectrophotographic detection of 10^{-5} g. of potassium, rubidium or cesium.²³

Allison states that the concentration of element 87, in the several minerals investigated, varies between 1 part in 10^{10} and 10^8 parts of the mineral.⁴ From the above deductions, it may be concluded that in order to secure spectroscopic evidence for the existence of element 87 a concentrate from 1–100 kg. of ore will be necessary, the quantity depending upon the nature of the mineral.

Summary

The ionization potential and the doublet separations of the principal series spectrum of element 87 have been evaluated by several independent methods. The values are not very concordant, but it may be assumed for purposes of further investigation that the ionization potential is approximately 4.11 ± 0.2 volts. In the spectrophotographic detection of the element, an intense line of approximate wave length 4260 ± 100 Å. is to be expected, followed by a much weaker line, of longer wave length, separated from the intense line by $550 \pm 50\mu$.

²³ These experiments were performed in the Chemistry Laboratories of the Washington Square College, New York University, during the summer of 1931.

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NON-METALLIC CATALYSTS FOR HYDROGENATION AND DEHYDROGENATION. II. THE CATALYTIC PROPERTIES OF CHROMIUM OXIDE

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In the first report on the specificity of oxide hydrogenation catalysts¹ it was pointed out that a number of difficultly reducible oxides catalyze the hydrogenation of carbon monoxide and other compounds containing the carbonyl group, but are quite inert toward activating ethylene and its homologs for hydrogenation. A continuation of this line of investigation has led to the discovery that amorphous chromium oxide constitutes an exception to the rule governing the behavior of oxide catalysts generally. In fact, the high activity of specially prepared samples of chromium oxide as catalysts for the hydrogenation of ethylene prompted a further study of the catalytic properties of this oxide and the effect of variations in the

¹ Vaughen and Lazier, *THIS JOURNAL*, 53, 3719 (1931).