

sets of results agree fairly well, except for the case of the equilibrium mixture, but at higher temperatures the difference is very marked. As may be seen from Fig. 2, according to our calculations, the heat capacity after reaching a maximum, descends asymptotically toward the equipartition value, which it reaches, within a few thousandths of a calorie, at a temperature of 100°K. We have been unable to discover the source of the large deviation, but suspect it lies in the evaluation of the sums involved.

For the sake of completeness, we have calculated the vibrational heat capacity at room temperature. Use is made of the same equation as in rotation, namely $C/R = (\sigma^2 d^2 \ln Q / d\sigma^2)$, but in this case we substitute vibrational energies in the expression for Q . With the

frequency assignments of Dennison (D. M. Dennison, *Astroph. J.* **62**, 84 (1925)) and assuming simple harmonic motion, we obtain $C_v^{(298.1)}/R = 0.296$. For the heat capacity of methane at room temperature, therefore, we have $3/2 R$ for translation, $3/2 R$ for rotation, R for $C_p - C_v$ and $0.296 R$ for vibration. Thus

$$C_p^{298.1} = 8.54 \text{ cal. mole}^{-1}.$$

The International Critical Tables gives $C_p = 8.47$ at 15°C, and at this temperature our calculated value would be 8.45.

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An Estimation of the Spectrum of the Element of Atomic Number 87

During the past two years I have been examining the optical spectra of mineral concentrates in an effort to identify the *raies ultimes* of the missing alkali element, eka-caesium. A comparison of alkali spectra shows that the principal series spectrum of this element will be characterized by a widely separated doublet in the red region, and a closer doublet in the violet. K. T. Bainbridge,¹ basing his computations on the similarity of the spectrum of Ra II with that of un-ionized eka-caesium, has estimated the wave-length of the $1^2S - 2^2P_2$ line to be $7600 \pm 200\text{A}$, and that the component of lesser intensity, $1^2S - 2^2P_1$, is further in the red at $8720 \pm 200\text{A}$. F. H. Loring² has made another estimate, based on Hick's equation for series spectra, which lead to values of 8061A for the $1^2S - 2^2P_2$ line, and 4831A as the wave-length of the $1^2S - 3^2P_2$ line. Both estimates of the $1^2S - 2^2P_2$ line place it in a region of poor photographic sensitivity, indicating that for purposes of identification, the $1^2S - 3^2P_2$ transition, though theoretically not the most persistent line in the spectrum of the element, will be more important than the true *raie ultime* in the red. As the approximated wave-lengths of the red line differ considerably from each other, corresponding doubt is placed on the estimate made by Loring of the wave-length of the line in the violet region. In general, a more exact knowledge of the position of the individual lines, together with independent estimates of the doublet separations, are desirable.

Unfortunately, the methods which led to the exact elucidation of the spectra of stripped atoms of the initial series of the periodic table are not applicable to the present case owing to the paucity of analyzed spectra in the 7th period. Spectral regularities in a group of elements, as observed by Ramage³ among the atomic weights of the alkalis, or by Hicks' for their atomic volumes,⁴ cannot be used for extrapolating the spectrum of eka-caesium because of a lack of generality in the correlations.

In an effort to estimate the spectrum of the missing alkali, I observed that for any spectral term T , in a periodic group of elements, the quantum defect Q , is roughly a linear function of the total quantum number n , of the valence electron. If Q is known, T can be calculated from the relationship: (1) $T = r^2 R / (n - Q)^2$, where R is the Rydberg constant and $r - 1$ is the degree of ionization of the atom. Though this relationship is not precise, it is singularly free from manifest exceptions (see Fig. 1). This generality has been tested and found to be true for the S , P , D , F , G and H levels of the neutral alkali atoms, the singlet and triplet S and P levels in the spectra of the

¹ K. T. Bainbridge, *Phys. Rev.* **34**, 752 (1929).

² F. H. Loring, *Chem. News* **140**, 178, 202, 242 (1930).

³ Ramage, *Proc. Roy. Soc.* **A70**, 1 (1902).

⁴ W. N. Hicks, *Proc. Roy. Soc.* **A83**, 226 (1910).

neutral alkaline earths, the doublet spectra of the neutral atoms of the elements of group III, for the *S*, *P* and *D* levels of the neutral copper, silver and gold atoms, and for the corresponding singlet and triplet levels of zinc, cadmium and mercury. The most marked curvature in the loci is observed in the case of the spectra of the singly ionized alkaline earth atoms, when the levels of radium are included. L. A. Turner⁵ observed that if the total quantum numbers assigned by Bohr to the first two groups of elements be given different integral values in the case of the elements of high atomic weight, then the corresponding quantum defects for the *S* and *P*

radium, from the energy levels of the known alkaline earths, other than radium, and comparing the result with the known spectrum of the element. If the relationship were exactly linear the first difference Δ , (see Table I) should be a constant and ϵ have the value zero. Since in this case the locus has a marked curvature, the value of Δ is not constant, and it may be assumed that the Δ of radium will probably differ from that of barium by as large an amount as the maximum deviation from constancy observed in that group. On this assumption, the quantum defects of the levels of radium were evaluated from the formula: (2) $Q_{Ra} = Q_{Ba} + \Delta_{Ba} + |\epsilon|_{\max}$. The

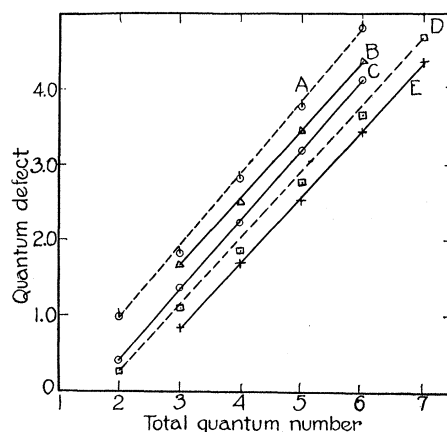


Fig. 1. *S* Levels for the elements of the first three groups. (Data from the Inter. Critical Tables 5, 392 (1929) 1st ed.) A, 2^2S_1 term for B I, Al I, Ga I, In I and Tl I ($n-1$, instead of n plotted, to avoid intersection with other curves); B, singlet system Mg I, Ca I, Sr I and Ba I (Be I and Ra I spectra not analyzed); C, 1^2S_1 term for Li I, Na I, K I, Rb I and Cs I; D, 1^2S term for Be II, Mg II, Ca II, Sr II, Ba II and Ra II; E, triplet system Be I, Mg I, Ca I, Sr I and Ba I. Dotted lines show marked curvature.

levels are, approximately, a linear function of the atomic number. At the end of his paper he states that H. N. Russell observed: "Straight lines will also be obtained if the quantum defects obtained from Bohr's quantum numbers are plotted against integers". The rule postulated above is more general and exact than Turner's formulation, and is better adapted for purposes of extrapolation in so far that the Bohr quantum numbers differ consistently by unity from element to element.

The utility of the rule, for estimating the spectrum of a heavy element, can be tested by calculating the principal series spectrum of

first transition of the principal series so estimated is 3950A for the major line, and 4500A for the component of lesser intensity; the wave-lengths of the observed lines being 3816A and 4683A, respectively.

From the law of spectroscopic displacement, the spectrum of eka-caesium may be expected to be similar to that of Ra II; hence, an equation of form (2) may be assumed valid for the extrapolation of its spectrum. The wave-lengths of the *raies ultimes* computed from the energy levels (see Table II) are:

⁵ L. A. Turner, Phil. Mag. 48, 384, 1010 (1924).

$1^2S-2^2P_2=7460\text{A}$, $1^2S-2^2P_1=8130\text{A}$, $1^2S-3^2P_2=4260\text{A}$, and $1^2S-3^2P_1=4310\text{A}$. These estimates are in closer agreement with the values of Bainbridge, than with those published by Loring. If Eq. (1) be investigated for the effect on the value of T produced by a small error in the estimation of Q , vis., (3) $\Delta T = -2r^2R\Delta n^*/(n^{*3}+2n^{*2}\Delta n^*)$, it will be

TABLE I. *Estimation of Ra spectrum (example 1^2S term).*

Element	n	Q	Δ	ϵ
Be	2	0.271		
Mg	3	1.097	0.826	-0.064
Ca	4	1.859	0.762	+0.157
Sr	5	2.778	0.919	-0.030
Ba	6	3.667	0.889	
Ra	7	(4.713)	Calc.	
		4.699	Observed	

observed that the levels of neutral atoms are much less sensitive than those of singly, or doubly ionized atoms. In (3), n^* is the effective quantum number, equal to $n-Q$.

The doublet separations in the principal series of the alkalis increases progressively with increase in nuclear charge. H. Bell⁶ has

shown that the separations can be accurately represented by empirical equations of the type: $(\Delta\bar{\nu})^{1/2} = m(N-N_0)$, and $\log \Delta\bar{\nu} = p \log N+q$, where N is the atomic number, and m , p , q and N_0 are constants. For element 87, the distance between the doublets, computed with the aid of these equations, are $1450\bar{\nu}$ and $467\bar{\nu}$ for the multiplets in the red and violet

TABLE II. *Estimated energy levels of RaII and Ek - Cs I.*

Level	Radium		Calc. for element 87
	Obs. $\bar{\nu}$	Calc. $\bar{\nu}$	
1^2S	82,862	83,880	32,930
2^2P_2	56,653	58,600	19,540
2^2P_1	61,510	61,680	20,560
3^2P_2	—	—	9,416
3^2P_1	—	—	9,750

regions, respectively. The separations obtained from the estimated 2^2P_j and 3^2P_j levels, $1100\bar{\nu}$ and $330\bar{\nu}$, are in fair agreement with the values calculated from Bell's equations.

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⁶ H. Bell, *Phil. Mag.* **36**, 337 (1918).

Excitation of High Optical Energy Levels. An Erratum

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In a letter to the Editor of the above title, line 12, page 194, read $58 \cdot 10^{-6}$ henrys instead of $6 \cdot 10^{-5}$ henrys.

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