

ANALYSIS OF SPECTRA ARISING FROM QUADRUPLY IONIZED TIN, $Sn V$

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Communicated March 7, 1928

It has been shown¹ for certain sequences of iso-electronic systems that when an electron transition takes place between two levels having the same total quantum number, the resulting lines are displaced to higher and higher frequencies by very nearly a constant value in passing from element

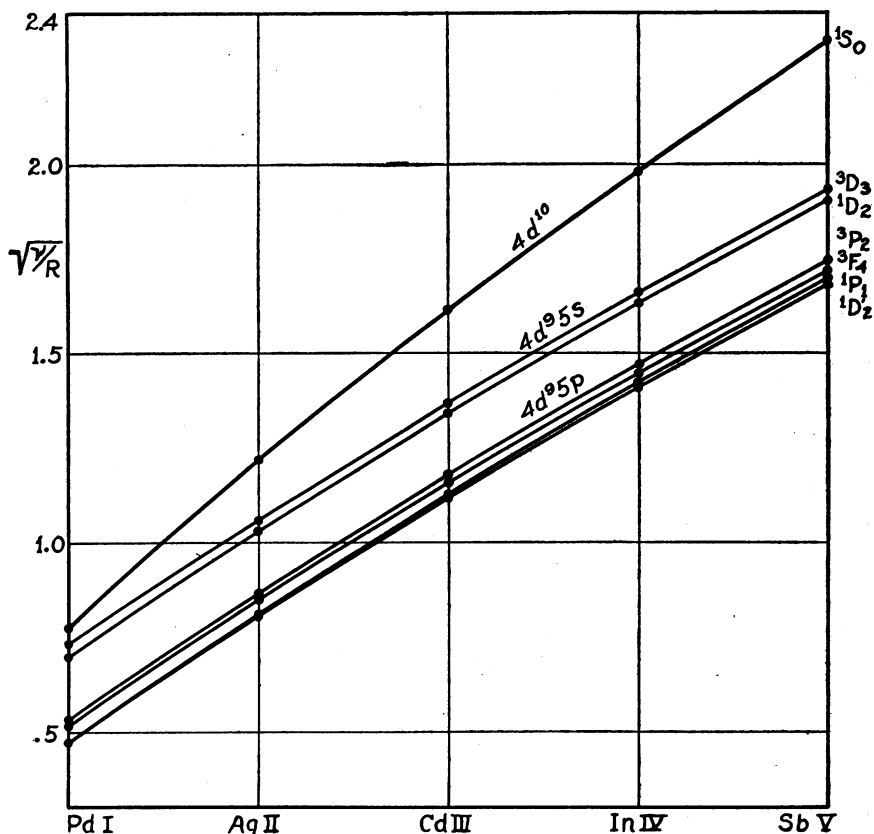


FIGURE 1
Moseley diagram.

to element. Applying this general rule to the spectra of Pd I² and Ag II², and guided by the Moseley type of diagram for the values of $\sqrt{\nu}/R$ of the terms, by term separations, and by relative intensities, we have been

able to identify most of the strong lines in the spectra of Cd III⁴, In IV⁴ and Sn V. The spectra reported in this paper were photographed in this laboratory with a new vacuum spectrograph.⁴ The lines arising from the transitions ³PD'F and ¹PD'F (4d⁹5p) into ³D and ¹D(4d⁹5s) are

TABLE 1
Tin V

4d ⁹ 5p	4d ¹⁰ ¹ S ₀ 0000	³ D ₂ 182586 2478	³ D ₃ 185064 6142	4d ⁹ 5s	³ D ₁ 191206 3025	¹ D ₂ 194231
		15				
		1160.81				
³ F ₄ 268733		86146.7				
		6	12			3
6411		1254.13	1294.34			1468.64
³ F ₃ 262322		79736.5	77259.4			68090.2
		0	10		4	7
11013		1101.94	1132.87		1217.60	1264.17
³ F ₂ 273335		90749.0	88271.3		82128.8	79103.3
		12	4?			4
		1089.40	1119.62			1247.70
³ D' ₃ 274379		91793.6	89316.2			80147.5
			12		10	7
5281		1155.90?	1189.98		1283.82	1335.70
³ D' ₂ 269098		86512.4	84035.0		77892.5	74867.0
	12		5		8	2
12067	355.66		1040.57		1111.62	1150.31
³ D' ₁ 281165	281167		96101.5		89958.8	86933.1
		15				2
		1302.23	1345.64?		1535.00
³ P ₂ 259377		76791.3	74313.9			65146.5
	10		10		3?	6
8620	373.14		1205.76		1302.23	1355.63
³ P ₁ 267997	267997		82935.2		76791.3	73766.3
					8	
5296					1218.21	
³ P ₀ 273293					82087.6	
		4	7			12
		1034.58	1061.80			1176.34
¹ F ₃ 279242		96657.0	94179.6			85009.4
			2		10	10
		1025.09		1093.98	1131.43
¹ D' ₂ 282615			97551.8		91409.4	88383.7
	15		3		3	6
	361.55		1092.58		1171.18	1214.24
¹ P ₁ 276590	276590		91526.4		85384.0	82356.0

found in the region 1000 to 1500 Å. The transitions ¹P₁, ³P₁, and ³D'₁- (4d⁹5p) into ¹S₀(4d¹⁰), the lowest energy level of the spectrum, were found at 361.55 Å, 373.14 Å and 355.66 Å, respectively, each within one Ångstrom of the wave-length predicted by an extrapolation of the ¹S₀ and ¹P₁ lines of

figure 1 from data already known for the first four elements in this sequence.

The intensities, wave-lengths and frequencies of the identified lines are given in table 1 together with the term values referred to ${}^1S_0(4d^{10})$ as zero. The line ${}^3D_2 - {}^3D'_3$ as it appears on our plates is much too strong, probably because it is coincident with another line due to some transition in a lower state of ionization. In the case of ${}^3D_2 - {}^3P_2$, a similar difficulty occurs due to the presence of another strong line from which it is not resolved on our plates. The lines due to transitions ${}^3D_3 - {}^3P_2$ and ${}^3D_1 - {}^3P_1$ have the same wave-length thus making it impossible to determine their relative intensities.

Throughout all five of the elements in this sequence the terms arising from $4d^95s$ are in the order that would be predicted from Hund's theory. According to Lande's interval rule the ${}^3D_{1,2,3}$ terms should have the interval ratio 2:3. They are found, however, to be more nearly 2:1. According to Hund's theory 3F_4 should be the lowest level arising from the d^9p configuration. Throughout this sequence as well as the corresponding sequence of the first long period⁵ 3P_2 lies deepest for this configuration. In both sequences the 3F_3 term lies deeper than 3F_4 . Similarly the ${}^3D'_2$ term lies below the ${}^3D'_3$ term in this sequence but in the reverse order in the other sequence. The terms 3F_4 and 3P_0 in these multiplets are each determined by the identification of a single line. In selecting this single line, relative intensities and predicted term separations were taken into consideration. The line ${}^3D_3 - {}^3F_4$ is, however, one of the strongest lines resulting from these transitions and its location can be predicted with considerable accuracy from a diagram similar to that used in the first long period.^{1b,6} The line selected for ${}^3D_1 - {}^3P_0$ is somewhat less certain but its intensity and the resulting term separations are reasonably satisfactory. Such terms can be fixed with greater certainty when the lines resulting from transitions from $4d^95d$ and $4d^96s$ to $4d^95p$ have been identified. These latter lines are, in general, much weaker and for several of these iso-electronic systems lie in the same region of the spectrum as lines resulting from the transitions from $4d^95p$ to $4d^95s$ of the once more ionized atoms. We hope soon to extend the analysis here reported for Tin V to Antimony VI.

¹ Gibbs and White, (a) *Physic. Rev.*, 29, 426 and 655, 1927; (b) these PROCEEDINGS, 13, 525, 1927.

² McLennan and Smith, *Proc. Roy. Soc.*, A112, 110, 1926; *Trans. Roy. Soc. Can.*, 20, III, 1926.

³ Kindly communicated to the authors in Nov., 1927, by A. G. Shenstone in advance of publication. *Physic. Rev.*, 31, 317, 1928. McLennan and McLay, *Trans. Roy. Soc. Can.*, 22, III, 1928.

⁴ Paper submitted to the *Physical Review* for publication by the authors in Jan., 1928, and presented at the New York Meeting of the American Physical Society, Feb.,

1928. (The transitions $4d^95p$ to $4d^95s$ of Cd III have since been published by McLennan, McLay and Crawford, *Trans. Roy. Soc. Can.*, 22, III, 1928.) They did not determine the $^1S_0(4d^{10})$ level. The independent identifications made in the two laboratories are in complete agreement. Paper by the authors will appear in the May number of the *Physical Review*.

⁵ A. G. Shenstone, *Physic Rev.*, 29, 380, 1927; Laporte and Lang, *Physic. Rev.*, 30, 378, 1927.

⁶ Gibbs and White, *Physic. Rev.*, 31, 309, 1928.

ON THE ENERGY AND ENTROPY OF EINSTEIN'S CLOSED UNIVERSE

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Communicated February 28, 1928

1. *Introduction*.—In a preceding article,¹ two principles have been proposed, expressed in a form valid for all sets of coördinates which seem suitable to serve as the analogues in general relativity for the first and second laws of thermodynamics. It is the purpose of the present article to apply these principles to the Einstein closed universe, regarded as filled with a perfect fluid, so as to obtain expressions which may be taken as representing the energy and entropy of this universe. In a following article we shall then use these expressions to investigate the equilibrium between radiation and matter in such a universe, a problem which has recently been attacked in a very stimulating manner by Lenz.²

In carrying out our computations, we shall not regard the pressure in the universe as necessarily negligible compared with the energy density, as has hitherto always been done in treatments of the Einstein universe. Our present necessity for abandoning this simplifying assumption arises from the fact that pressure and energy density are necessarily of the same order of magnitude for the case of radiation, and this rules out the simplification in a treatment of the equilibrium between matter and radiation. Owing to this fact that we do not neglect the pressure, the expression that we obtain for the energy of the universe will differ from that previously obtained by Einstein³ with the use of the simplifying assumption. Our expression for energy also differs from that tacitly taken by Lenz for his treatment of the equilibrium between radiation and matter, but our expression for the entropy turns out to be the same as that which he assumed.

2. *Metrical Properties of the Einstein Universe*.—Before we can apply the laws of thermodynamics to the Einstein universe, we must consider