

EXTENSION OF DOUBLET LAWS IN THE FIRST LONG PERIOD TO CHROMIUM AND MANGANESE¹

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Communicated October 30, 1926

We have already shown² that the regular and irregular doublet laws may be applied to stripped atoms of the first five elements in the first long period of the periodic table. Recently secured data on chromium and manganese in the extreme ultra-violet have made it possible to extend these laws to Cr_{VI} and Mn_{VII}. In view of data reported by Lang³ on elements in this period it seemed desirable to repeat our observations on vanadium to see whether the lines we had selected for the V_V doublet were correct or not, and to secure more accurate measurements of their wave-lengths.

A new photograph taken by using vanadium electrodes containing considerable carbon showed, unmistakably, only one line of the regular doublet at $\lambda = 1680.26$, the other being masked by several carbon lines, especially by a strong carbon doublet of the second order. A fairly strong vanadium line is found on this plate at $\lambda = 1722.51$ which is the one selected by Lang as the other member of this doublet. The separation between $\lambda = 1680.26$ and $\lambda = 1722.51$ does not yield a plausible screening constant, nor does it show the anticipated progression of $\Delta\lambda$. Since our earlier plate contained but few carbon lines it seemed evident that the line found at $\lambda = 1715.82$ with $\nu = 58281.1$, was due to vanadium. As that plate was not in excellent focus at this point a new photograph was made using a very pure specimen of vanadium which was very kindly given to us by Dr. A. S. King of the Mt. Wilson Observatory. This plate proved to be in excellent focus in this region with practically no carbon lines in evidence and showed a comparatively strong pair of lines in the same place as our original plate. With new secondary standards now available,⁴ the same two lines were measured very accurately and are given at $\lambda = 1680.26$ and 1716.74 with the separation of $\Delta\nu = 1264.7$, this wave-length separation being only 0.02 A.U. different from that given in our first report.² The new measurements of the short wave-length line corresponds almost exactly with a line recorded earlier by Lang⁵ in his measurements of the vanadium spark lines in vacuum. That our choice of lines for this doublet is correct is shown not only by the values of the screening constant and of $\Delta\lambda$ as can be seen in table 2, but also by the same frequency separation arising from jumps from the $4^2P_{1,2}$ levels to the 3^2D_2 level⁶ whose frequencies we have already given in another report.⁷

As heretofore by an almost linear extrapolation of the frequency of these

doublets and by a similar extrapolation of the screening constant it was then possible to predict the approximate locations and the frequency separations of the corresponding doublets of Cr_{VI} and Mn_{VII}. Recent spectrograms of these elements, in sharp focus in these regions, enabled us to identify these doublets with a high degree of certainty. The frequencies of these lines are given in table 1.

TABLE 1
IRREGULAR *N* DOUBLETS
 $4^2S_1 - 4^2P_1$

	LANG ²	AUTHORS	DIFF.
K _I		12985.1	12206.5
Ca _{II}		25191.6	
Sc _{III}		36565.3	11373.7
Ti _{IV}	(47542)	47533.3	
V _V	(58048)	58249.9	10968.0
Cr _{VI}	(66756)	68713.8	
Mn _{VII}		78913.5	10716.6
			10463.9
			10199.7

TABLE 2
REGULAR *N* DOUBLETS
 $4^2P_1 - 4^2P_2$

	LANG ²	$\Delta\nu$	AUTHORS	$\sqrt{\Delta\nu/0.0456}$	<i>s</i>	$\Delta\lambda$
K _I			57.7	5.964	13.036	34.07
Ca _{II}			222.8	8.360	11.640	34.81
Sc _{III}	(474)		474.3	10.09	10.91	35.02
Ti _{IV}	(821)		817.5	11.57	10.43	(35.8)35.57
V _V	(1462)		1264.7	12.91	10.09	(42.3)36.48
Cr _{VI}	(2367)		1821.5	14.15	9.85	(51.3)37.58
Mn _{VII}			2464.7	15.25	9.75	38.38

Not only the consistent decrease in the values of the screening constant, and the small but systematic increase in $\Delta\lambda$, but also the uniform progression in the frequencies of the principal doublets $4^2S_1 - 4^2P_{1,2}$ throughout the first seven elements of this period give a beautiful confirmation of the validity of the regular and irregular doublet laws as applied to stripped atoms.

We wish to express our sincere thanks to Dr. I. S. Bowen for using the vacuum spectrograph at the Norman Bridge Laboratory to secure several of the spectrograms used in this report and to Mr. C. W. Gartlein for re-determining the frequency separation of the Ti_{IV} doublet whereby he finds the same separation as recorded before.²

¹ The assistance of a grant to the first author from the Heckscher Research Foundation of Cornell University which enabled us to obtain the results described in this report is gratefully acknowledged.

² Gibbs, R. C., and White, H. E., these PROCEEDINGS, 12, p. 448 (1926).

³ Lang, R. J., *Nature*, 118, p. 119 (July 24, 1926).

⁴ Bowen, I. S., and Ingram, S. B., *Physic. Rev.*, 28, p. 444 (1926).

⁵ Lang, R. J., *Phil. Trans. Roy. Soc.*, A224, p. 388 (1924).

⁶ Following the notation of Russell, H. N., and Saunders, F. A., *Astrophys. J.*, 61, p. 66 (1925).

⁷ Gibbs, R. C., and White, H. E., these PROCEEDINGS, 12, p. 598 (1926).

IONIC MOBILITIES IN AMMONIA-HYDROGEN MIXTURES AND AN ANOMALOUS EFFECT OF AMMONIA

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Communicated November 11, 1926

Introduction.—In a previous paper¹ the writer has pointed out the advantages of studying mobilities in mixtures using hydrogen gas as one of the constituents. Some two years ago the writer and Miss Ashley² had determined mobilities in mixtures of ammonia and air. The results obtained were not completely in accord with the later work in mixtures inasmuch as they gave a variation of mobility with concentration different from that found in other mixtures studied. The results were, furthermore, not certain at low concentrations of NH_3 because of the relatively small difference in ionic mobilities for ions in air and NH_3 , and it is just in the region of small concentrations of NH_3 that the results are interesting. Finally as brass electrodes were used and these were acted on by the NH_3 giving contact potential differences which had to be allowed for it was felt desirable to repeat measurements on an ammonia mixture free from these difficulties. Measurements were accordingly made in ammonia-hydrogen mixtures using gold-plated electrodes with the surprising results detailed below.

Experimental Procedure.—The ionization chamber, the gauze and the plate were those used for NH_3 -air² mixtures except that the gauze and plate had been gold plated as they were in the H_2 -ether mixture work.¹ The H_2 was purified as before. The ammonia was generated by dropping a concentrated NaOH solution onto Baker's analyzed c.p. NH_4Cl . It passed through a trap cooled to -25°C . by an alcohol bath, through a meter-long tube of finely powdered NaOH , and into a bulb cooled in liquid air where it was frozen out. The mixtures of the gases were obtained by exhausting the bulb of frozen NH_3 and the ionization chamber down