CERTAIN SPECTRA IN THE VANADIUM I ISO-ELECTRONIC SEQUENCE

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Abstract

Displacement of multiplets in the iso-electronic sequence which begins with the arc spectrum of vanadium.—Regular displacements were observed for analogous quartets and sextets in the spectra of Mn III, Fe IV, Co V and Ni VI, continuing those already known for V I and Cr II. In addition a new sextet sequence has been found for V I to Co V. The configuration changes investigated were $3d^4\,4p$ to $3d^4\,4s$, $3d^4\,4d$ to $3d^4\,4p$, $3d^4\,4p$ to $3d^5$ and $3d^3\,4sp$ to $3d^3\,4s^2$.

Moseley diagrams and the irregular doublet law.—The irregular doublet law was applied to systems of sextets and quartets due to electronic changes in atoms having five electrons in outer shells. When the change did not involve a change in total quantum number, the law was closely followed.

Centroid diagram.—Shifts of energy levels for sextets and quartets of ($P^\circ\ D^\circ\ F^\circ$) $3d^4\,4p$ have been calculated for V I to Co V, using the centroid method. Values are not absolute because not all the levels of this configuration are known. But relative values are useful for predicting higher states in the sequence.

Landé interval rule.—Typical tests of the Landé interval rule are given.

Regular doublet law.—The $(\Delta\nu)^{1/4}$ is linear with atomic number in some cases, but not in all.

Tables are given for the new lines and new term values.

THE regular and irregular doublet laws have been shown to hold for several iso-electronic sequences in the first long period of the table of elements.[1,2,3]. This report gives the results of a further application of these laws to the iso-electronic sequence which starts with the arc spectrum of vanadium, and also of an attempt to find radiated lines due to changes in energy level involving L values which are less than the maximum.

The neutral vanadium atom has, in addition to the closed sub-shells of electrons called $1s^2\ 2s^2\ 2p^6$ and $3s^2\ 3p^6$, five valence electrons which, for this iso-electronic sequence, may have the configuration $3d^3\ 4s^2$. Lines in the arc spectrum of vanadium will be due then, to excitation of any one or more of these valence electrons and their subsequent return to a lower energy state. Several sextets and quarters have previously been found in this spectrum, due to changes in electron configuration from $3d^44p$ to $3d^44s$, $3d^44p$ to $3d^5$, $3d^34sp$ to $3d^34s^2$, $3d^34sp$ to $3d^44s$ and $3d^44p$ to $3d^34s^2$.[4,5,6].

[1] Gibbs and White, Phys. Rev. **29**, 426 and 655 (1927); Gibbs and White, Phys .Rev. **33**, 157 (1929).
[2] Gibbs and White, Proc. Nat. Acad. Sci. **13**, 525 (1927); and **12**, 598 and 448 (1926)
[3] White, Phys. Rev. **33**, 538, 672 and 914 (1929).
[4] W. F. Meggers, J. of Wash. Acad. of Sci. **13**, 317 (1923); **14**, 151 (1924).
[5] O. Laporte, Die Naturwissenschaften **11**, 779 (1923).
[6] H. N. Russell, Astrophys. J. **66**, 184 (1927).

Of the second member of this sequence, the first spark spectrum of chromium, only quartets and sextets of the electron changes $3d^44p$ to $3d^44s$ and $3d^44p$ to $3d^5$ have been reported.[6,7,8]. Since the chromium atom which is emitting the first spark spectrum has lost one electron, it will have as many electrons outside the completed sub-shells as the neutral vanadium atom. Hence the spectra have been found to be similar in several respects, though the relative order of energy levels may differ. This will be shown later in one of the graphs. Very few data have been published about the remaining spectra of

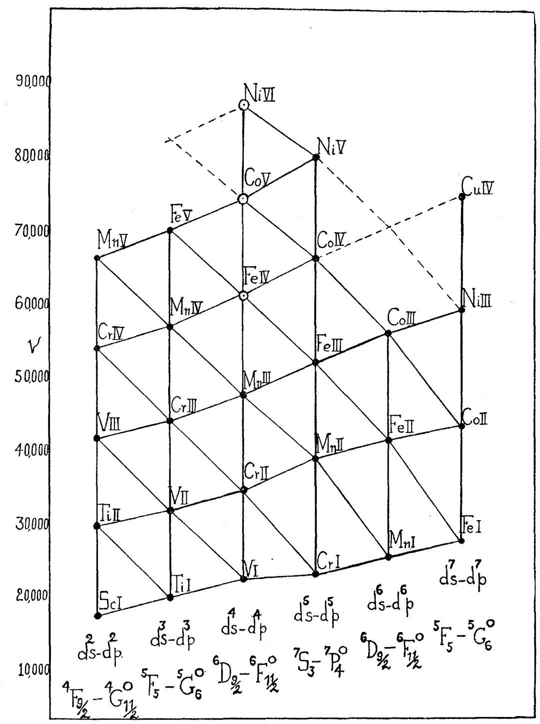

Fig. 1. Regular displacement of multiplets.

this sequence, Mn III, Fe IV, Co V and Ni VI. One sextet group in Mn III, $3d^44s\ {}^6D-3d^44p\ {}^6F^\circ$, has been identified.[2]

According to the present theory of atomic structure and line spectra, a space quantization of the electrons $3d^44s$ give the following energy levels;— ${}^2(S, D, G)$, ${}^{2,4}(P, F)$, ${}^2(S, D, F, G, I)$, ${}^{2,4}(P, D, F, G, H)$ and ${}^{4,6}(D)$. Of these, only the ${}^{4,6}(D)$ which are involved in the emission of the more intense lines, have been considered in this investigation. Similarly, from the $3d^44p$ configuration only those levels which are derived from the ${}^5D$ level of a d^4 configuration, have been studied, that is ${}^{4,6}(P^\circ, D^\circ, F^\circ)$. In the next higher configuration, $3d^44d$, we have levels ${}^{4,6}(S, P, D, F, G)$ from the same $d^4\ {}^5D$ limit. In the d^5

[7] Meggers, Kiess and Walters Jr., J. Opt. Soc. Amer. **9**, 361 (1924).
[8] C. C. Kiess and O. Laporte, Science **63**, 234 (1926).

configuration there are levels $^4(D, G)$ and ^6S from the same limit. Since there are two possible methods of ionizing an atom having valence electrons d^4s, one by the removal of an s electron and the other by the removal of a d electron, we might build a five-electron system on the $3d^34s$ configuration, whose lowest energy levels should be $^5(P, F)$. The addition of an s electron to this configuration gives levels $^{4,6}(P, F)$ of the $3d^34s^2$ configuration, while the addition of a p electron gives $3d^34sp\ ^{4,6}(S^\circ, P^\circ, D^\circ, F^\circ, G^\circ)$. This report includes the wave-lengths of a few multiplets due to the electronic change $(3d^34s^2 - 3d^34sp)$.

Displacement of Multiplets

The method employed for predicting the spectral regions in which these multiplets should be found, is that of Gibbs and White.[1,2] Figure 1 is in part a reproduction of their graph showing the regular displacement of multiplets with increasing atomic number but the same number of outer electrons, and with increasing number of d electrons in the incompleted sub-shell but in the same state of ionization. For one electron transition, $3d^44s - 3d^44p$, and one multiplet group, $^6D - {^6F^\circ}$, radiated frequencies have been found for V I[4], Cr II[7] and Mn III[2] with separations of about 13,000 cm^{-1}. From this regularity one may expect that the corresponding line for Fe IV will be at about 61,000 cm^{-1}, for Co V at about 74,000 cm^{-1} and for Ni VI at about 87,000 cm^{-1}. These points are indicated by circles instead of solid dots in Figure 1. In Fe V the line $3d^34s\ ^5F_5 - 3d^34p\ ^5G^\circ_6$ found by White[3] at 69,905 cm^{-1} fits into this diagram, as do $3d^54s\ ^7S_3 - 3d^54p\ ^7P^\circ_4$ for Co IV and Ni V at 66,573 cm^{-1} and 80,376 cm^{-1} respectively, both determined by Morell.[9] With these frequencies and those now identified for lines $^6D - {^6F^\circ}$ in Fe IV, Co V and Ni VI, it is possible to predict with a fair degree of accuracy the most intense lines in parallel sequences. For instance, the line $3d^34s\ ^5F_5 - 3d^34p\ ^5G^\circ_6$ of Co VI should be at 82,500 cm^{-1} and $3d^64s\ ^6D_{9/2} - 3d^64p\ ^6F^\circ_{11/2}$ of Ni IV at 70,700 cm^{-1}.

Photographs taken with a vacuum spectrograph in the regions indicated for the five-electron sequences, show the head line of $(^6D - {^6F^\circ})$ $(3d^44s - 3d^44p)$ from Fe IV at 61,312 cm^{-1}, from Co V at 74,312 cm^{-1} and from Ni VI at 87,388 cm^{-1}. These are plotted in Figure 2. In the same manner, from a knowledge of quartets and sextets in the spectra of V I and Cr II, corresponding multiplets have been found for the remainder of the sequence. Some of these are shown in Fig. 2. This completes the multiplet groups produced by the electron change $3d^44s - 3d^44p$, which approach the limit $3d^4\ ^5D$, a multiplet arising from the configuration $3d^4$ of the corresponding atom, in the next higher state of ionization.

Another possible configuration change involved in this same iso-electronic sequence is from $3d^44p$ to $3d^5$. Since ^6S is the only sextet in the $3d^5$ configuration the only probable sextet group of lines of any intensity is $^6S - {^6P^\circ}$. This results in three lines, $^6S_{5/2} - {^6P^\circ}_{3/2,5/2,7/2}$ whose term differences are already known for all the elements in the sequence, having been found in one of the

[9] Morell, Thesis, Cornell, 1928.

sets of multiplets mentioned above; i.e ($3d^44s-3d^44p$) ($^6D-^6P°$). This group of lines has been followed through the sequence except in Ni VI, where the lines should appear at about 318A. At this very short wave-length the lines are so faint and the probable error in reciprocal cm so large, that this group has been omitted from the tables of wave-lengths and term values, although two lines were found approximately in this position. Lines due to two more changes in electronic configuration, $3d^44p-3d^44d$ and $3d^34s^2-3d^34sp$, have been found for the sequence to Co V. The group $^6F°-^6G$ from the $3d^44p-3d^44d$ change, involving the largest L values, contains the strongest lines of the first configuration change, though much weaker than the strong lines of the $3d^44s-3d^44p$ groups. For Mn III two additional sextet groups, $^6F°-^6F$ and $^6F°-^6D$, have been found for $3d^44p-3d^44d$.

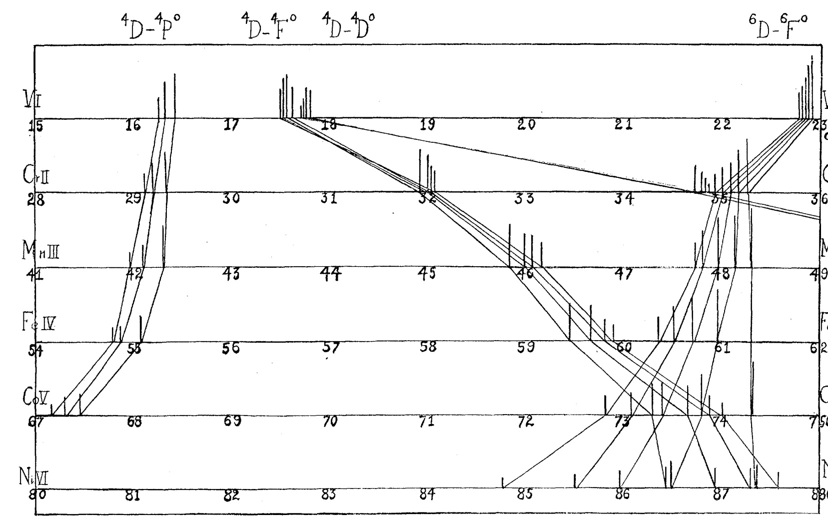

Fig. 2. Displacement of multiplets. Iso-electronic sequence $3d^44s-3d^44p$.

In Figure 2 the nearly linear increase in radiated frequency with increasing atomic number, can be observed from the small change in direction of the connecting lines. This is also true of other multiplets not shown in this chart. A $3d^44p-3d^44d$ change involves approximately 20,000 cm^{-1} shift in frequency from any element to the next higher in the sequence, a $3d^44s-3d^44p$ change involves 13,000 cm^{-1} shift and a $3d^34s^2-3d^34sp$, about 13,500 cm^{-1}. Where the change in electronic configuration involves a change in total quantum number, the lines are displaced somewhat irregularly toward the shorter wave-lengths. In the case of a $3d^5-3d^44p$ change the displacement is about 60,000 cm^{-1} between any two members of the sequence.

One of the tests which has been used throughout to distinguish between lines due to high and low stages of atomic ionization, is apparently not absolutely reliable when adjacent lines belong to different sequences. In general, the presence of an inductive resistance in series with the spark gap very greatly reduces the intensity of the high ionization lines.[10,11]. In the manganese spectrum the $(3d^44p-3d^44d)$ $(^6F^\circ-^6G)$ group of Mn III is closely adjacent to $(3d^34s-3d^34p)$ $(^5F-^5G^\circ)$ of Mn IV and $(3d^24s-3d^24p)$ $(^2F-^2F^\circ)$ of Mn V. An inductance which is sufficient nearly to efface the strongest line and completely to efface the other lines of the Mn III group, reduces the intensities of the lines of the Mn IV and Mn V groups to a much less extent. Without the inductance the intensities of the latter two groups are nearly the same as that of the strongest Mn III line in the multiplet under discussion.

Irregular Doublet Law

These same data may be combined in another manner to illustrate the irregular doublet law. Bowen and Millikan[12] have shown that the irregular doublet law for x-rays may be transferred to doublets of the second and third periods which are due to one-electron systems. Gibbs and White[1,2,3,13]have extended this application to doublets of the fourth, fifth and sixth periods and to triplets, quartets and quintets in the first and second long periods of the elements. Table I gives the results of a test of this law for systems of lines due to five electrons in outer shells, quartets and sextets having the largest L

Table I. *Irregular doublet law.* Values of $\nu^{1/2}$ referred to $3d^4\ ^5D_0$ of V II, Cr III, Mn IV, etc.

Config.	T.	V I	Δ	Cr II	Δ	Mn III	Δ	Fe IV	Δ	Co V	Δ	Ni VI
$3d^44s$	$^6D_{9/2}$	228	120	348	122	470	122	592	122	714	122	836
$3d^44p$	$^6F^\circ_{11/2}$	171	122	293	122	415	123	538	122	660	122	782
$3d^44d$	$^6G_{13/2}$	90	126	216	121	337	122	459	122	581	122	703
$3d^5$	$^6S_{5/2}$	182	184	366	162	528	150	678	143	821	129	(950)
Values of $\nu^{1/2}$ referred to $3d^4\ ^5D_0$ of V II, Cr III, Mn IV, etc.												
$3d^44s$	$^4D_{7/2}$	214	124	338	123	461	124	585	122	707	123	830
$3d^44p$	$^4F^\circ_{9/2}$	167	120	287	121	408	123	531	122	653	123	776
Values of $\nu^{1/2}$ referred to $3d^34s\ ^5F_1$ of V II, Cr III; etc.												
$3d^34s^2$	$^4F_{9/2}$	237.5	77.5	315	77.5	392.5	77.5	470	78	548		
$3d^34sp$	$^4G^\circ_{11/2}$	158	78	236	77.5	313.3	77.3	390.6	77.8	468.4		

values being selected to represent each system. Graphically this can be shown in a Moseley diagram, as in Fig. 3. In this figure are plotted the square roots of term values referred to $3d^4\ ^5D_0$ of the corresponding atom in the next higher state of ionization. In the case of V I, for instance, Russell's[14] value of 52,300 for the limit of $3d^44s\ ^6D_{1/2}$ was assumed, giving 51,988 for $3d^44s\ ^6D_{9/2}$. The square root of 51,988, that is 228, was then used as the starting point for the graph. Knowing the radiated frequency of $3d^44s\ ^6D_{9/2}-3d^44p\ ^6F^\circ_{11/2}$ we may

[10] Fowler, Phil. Trans. Roy. Soc. **A225,** 1 (1925).

[11] Gibbs, Vieweg and Gartlein, Phys. Rev. **34,** 406 (1929).

[12] Bowen and Millikan, Phys. Rev. **24,** 209 (1924); Phys. Rev. **25,** 295, and **26,** 150 (1925); **27,** 144 (1926).

[13] Gibbs and White, Proc. Nat. Acad. Sci. **12,** 551 and 675 (1926); **14,** 345 and 559 (1928); Phys. Rev. **29,** 359 (1927); **31,** 520 (1928); **33,** 157 (1929).

[14] Russell, Astrophys. J. **66,** 233 (1927).

determine the term value of $3d^4p\ {}^6F^{\circ}_{11/2}$ referred to the same limit. The square root of this term value gave the first point on the $3d^44p\ {}^6F^{\circ}_{11/2}$ curve. For the Cr II spectrum Russell's approximate value of 122,000 for $3d^44s\ {}^6D_{1/2}$ referred to $3d^4\ {}^5D_0$ of Cr III, was used and the square roots of term values for $3d^44s\ {}^6D_{9/2}$ and $3d^44p\ {}^6F^{\circ}_{11/2}$ were determined as in the case of V I. The limits of the sextet series are not known for Mn III, so an extrapolated number for the square root of the term value was read from the graph, assuming that

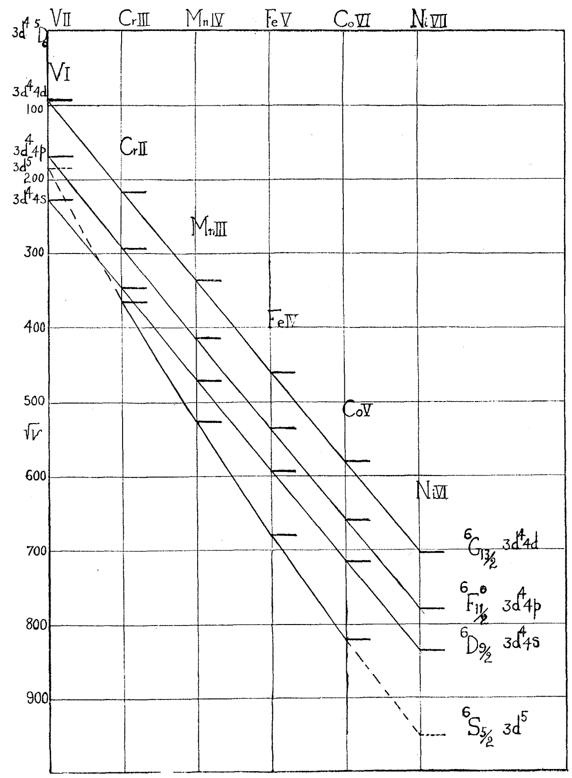

Fig. 3. Moseley Diagram. $\nu^{1/2}$ vs. atomic number.

$3d^44s\ {}^6D_{9/2}$ could be represented by a straight line. This assumption was made on the strength of curves for four sequences reported by White.[3] Since the radiated frequency $3d^44s\ {}^6D_{9/2}-3d^44p\ {}^6F^{\circ}_{11/2}$ is known, the square root of the term value for $3d^44p\ {}^6F^{\circ}_{11/2}$ can be readily calculated. A continuation of this method for the remaining elements in the sequence resulted in parallel lines, showing that $\Delta\nu^{1/2}$ is constant, independent of the atomic number, as required by the irregular doublet law. When the same method was applied to the lines $3d^44d\ {}^6G_{13/2}$ and $3d^5\ {}^6S_{5/2}$ corresponding curves were obtained. In the former case the curve is very nearly parallel to those for $3d^44p\ {}^6F^{\circ}_{11/2}$ and $3d^44s\ {}^6D_{9/2}$,but not in the latter case. Since the irregular or screening doublet law in x-ray spectra holds only for levels between which the transition involves no change in total quantum number of the electrons, the line representing

$\nu^{1/2}$ for $3d^5\ {}^6S_{5/2}$ should not be parallel to those for $3d^44s$, $3d^44p$ and $3d^44d$, in all of which the total quantum numbers of all the electrons involved in the electronic configuration, are the same.

The term values for the quartets, recorded in Table I, are referred to the lowest level, $3d^4\ {}^5D_0$, of the sextet limits, and the same method was used in calculating the $\nu^{1/2}$ for successive elements. A slightly different method was

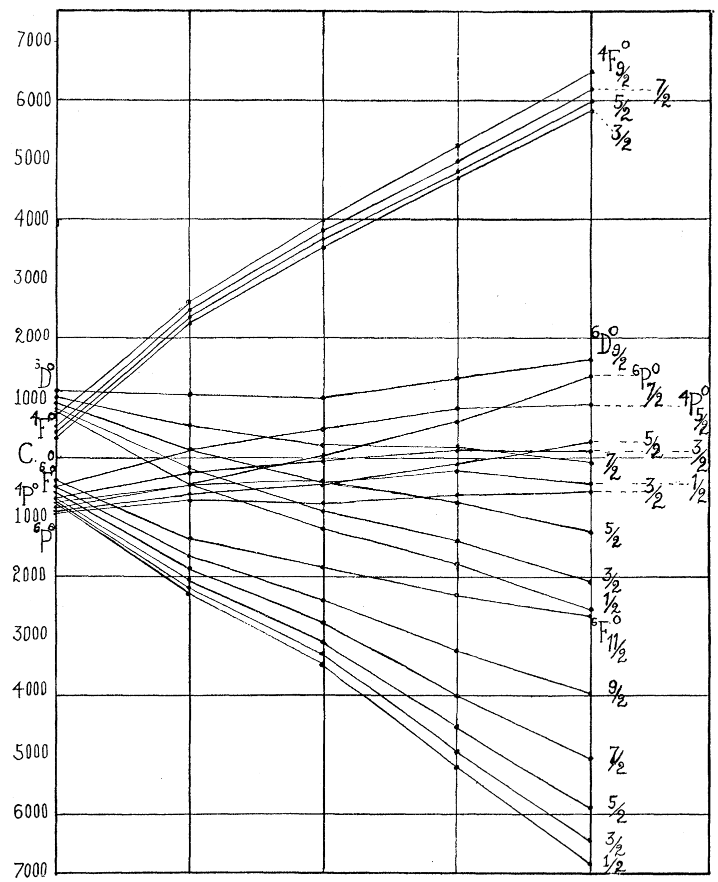

Fig. 4. Shift of Energy Levels. $3d^44p\ {}^4(F^\circ P^\circ)\ {}^6(P^\circ D^\circ F^\circ)$

used for the second set of quartets in Table I, because the limits were known only in the case of $3d^34s^2\ {}^4F_{9/2}$ of V I. For convenience, the reference level taken is $3d^34s\ {}^5F_1$ of V II rather than the actual limit, $3d^34s\ {}^5F_5$. From the radiated frequency $3d^34s^2\ {}^4F_{9/2} - 3d^34sp\ {}^4G^\circ_{11/2}$ and the known term value of $3d^34s^2\ {}^4F_{9/2}$, the term value for $3d^34sp\ {}^4G^\circ_{11/2}$ can be found and hence the $\nu^{1/2}$ for each level. Assuming that $\Delta\nu^{1/2}$ is constant and knowing the values of $3d^34s^2\ {}^4F_{9/2} - 3d^34sp\ {}^4G^\circ_{11/2}$ for the remainder of the sequence, values for $\nu^{1/2}$ can be calculated. With these values plotted for both $3d^34s^2\ {}^4F_{9/2}$ and $3d^34sp$ ${}^4G^\circ_{11/2}$, the lines are observed to be straight, which is in agreement with the results for the sextets and the first set of quartets having the same total quantum number. The one exception is the $3d^5\ ^6S_{5/2}$ line, already mentioned, which is related to the others by means of an electronic change involving a change in total quantum number and hence not a violation of the irregular doublet law.

A comparison of Table I with Fig. 3, shows that $3d^34s^2\ ^4F_{9/2}$ represents the lowest energy level of V I, but does not for the remainder of the sequence. Instead, $3d^5\ ^6S_{5/2}$ has dropped slightly below $3d^34s^2\ ^4F_{9/2}$ for Cr II and with rapidly increasing frequency difference, continues to be the lowest level for the rest of the sequence. The level $3d^5\ ^6S_{5/2}$ for Ni VI has not been definitely determined, but there is small probability that the $\nu^{1/2}$ will not be in the position indicated by the dotted line in Fig. 3.

TABLE II. *Landé interval rule.* Term separations of $3d^44s$ in cm^{-1}.

Spectrum	$^6D_{9/2}$ — $^6D_{7/2}$	$^6D_{7/2}$ — $^6D_{5/2}$	$^6D_{5/2}$ — $^6D_{3/2}$	$^6D_{3/2}$ — $^6D_{1/2}$	
V I	113 (4.5)	91 (3.6)	67 (2.7)	41 (1.6)	(4)
Cr II	192.7 (4.5)	156 (3.6)	115 (2.7)	70.8 (1.7)	(7)
Mn III	296 (4.5)	241 (3.7)	180 (2.7)	132 (2.0)	
Fe IV	594.5 (4.5)	476 (3.6)	341 (2.6)	253 (1.9)	
Co V	851 (4.5)	678 (3.6)	524 (2.7)	314 (1.66)	
Ni VI	1272 (4.5)	976 (3.5)	642 (2.3)	341 (1.2)	
Theory	4.5	3.5	2.5	1.5	

	$^4D_{7/2}$ — $^4D_{5/2}$	$^4D_{5/2}$ — $^4D_{3/2}$	$^4D_{3/2}$ — $^4D_{1/2}$	
V I	137 (3.5)	102 (2.6)	63 (1.6)	(4)
Cr II	226 (3.5)	166.7 (2.6)	103 (1.6)	(7)
Mn III	328 (3.5)	241 (2.6)	146 (1.6)	
Fe IV	448 (3.5)	307 (2.4)	184 (1.4)	
Co V	626 (3.5)	428 (2.4)	265 (1.5)	
Ni VI	852 (3.5)	625 (2.6)	373 (1.5)	
Theory	3.5	2.5	1.5	

Centroid Diagram

Greater detail in analysing the shift of energy levels is presented in Fig. 4. The zero line in this figure is the centroid of the configuration under consideration for each element, in so far as the levels have been determined. Vertical distances are the frequency differences between this centroid and each level. The centroid, according to the usual method[15] is calculated as the mean of all the levels weighted in proportion to $2j+1$, where j is the inner quantum number of the level. The final grouping of the levels in Co V indicates a possible coupling which differs from the Russell-Saunders but is not sufficiently different to follow the jj coupling of much heavier elements.[15,16] Addition of other quartet and doublet levels, now unknown, will change the values of the levels given, but should not appreciably change their relative shift. The relative values are useful in predicting higher states in the sequence.

The Landé Interval Rule

The Landé interval rule was found useful in locating most of these multiplets. Though it does not hold for all cases, Table II gives a typical illustration of the extent of variation in the spectra studied. In this table term separations are given in reciprocal centimeters; in brackets under each separation is a number to be compared with the theoretical ratios of term separations given at the bottom of the table. The spread of the multiplets, which appears

Table III. *Regular doublet law.*

			$\Delta\nu$	$\Delta\nu^{1/4}$	s
$3d^44s$	$^4D_{7/2}-^4D_{5/2}$	V I	137	3.42	14.36
		Cr II	226	3.88	14.20
		Mn III	328	4.28	14.18
		Fe IV	448	4.61	14.34
		Co V	626	5.02	14.31
		Ni VI	852	5.41	14.32
$3d^44s$	$^6D_{9/2}-^6D_{7/2}$	V I	113	3.26	17.85
		Cr II	193	3.73	18.22
		Mn III	296	4.16	18.50
		Fe IV	594	4.92	18.30
		Co V	851	5.41	18.55
		Ni VI	1272	5.98	18.68
$3d^44p$	$^6F^\circ_{11/2}-^6F^\circ_{9/2}$	V I	142	3.46	17.65
		Cr II	287	4.12	17.62
		Mn III	490	4.71	17.78
		Fe IV	935	5.54	17.63
		Co V	1374	6.10	17.62
		Ni VI	2183	6.82	17.50
$3d^44d$	$^6G_{13/2}-^6G_{11/2}$	V I	99	3.15	17.83
		Cr II	159	3.56	18.14
		Mn III	317	4.24	18.05
		Fe IV	575	4.90	17.96
		Co V	929	5.53	17.93

[15] Mack, Laporte and Lang, Phys. Rev. **31**, 748 (1928).
[16] Mack, Phys. Rev. **34**, 17 (1929).

TABLE IV. *Configuration change* $3d^34s^2-3d^34sp$.

Mn III.

s^2 \ sp	$^4F_{9/2}$	632	$^4F_{7/2}$	460	$^4F_{5/2}$	340	$^4F_{3/2}$
$^4G^\circ_{11/2}$	55850.6 50 1790.49						
495							
$^4G^\circ_{9/2}$	55355.7 23 1806.50		55987.9 50 1786.10				
338							
$^4G^\circ_{7/2}$	55017.6 18 1817.60		55650.2 25 1798.05		56110.1 40 1782.19		
292							
$^4G^\circ_{5/2}$					55818.2 12 1793.57		56158.3 6 1780.68

Fe IV.

s^2 \ sp	$^4F_{9/2}$	824	$^4F_{7/2}$	626	$^4F_{5/2}$	450	$^4F_{3/2}$
$^4G^\circ_{11/2}$	68268.2 40 1464.81						
595							
$^4G^\circ_{9/2}$	67673.2 5 1477.69		68496.9 40 1459.92				
425							
$^4G^\circ_{7/2}$	67246.8 5 1487.35		68071.7 37-x 1469.04		68697.4 25 1455.66		
356							
$^4G^\circ_{5/2}$					68341.0 4 1463.25		68791.4 15 1453.67

Co V.

s^2 \ sp	$^4F_{9/2}$	1088	$^4F_{7/2}$	966	$^4F_{5/2}$	544	$^4F_{3/2}$
$^4G^\circ_{11/2}$	80844.0 20 1236.95						
846							
$^4G^\circ_{9/2}$	80198.2 8 1246.91		81186.6 15 1231.73				
532							
$^4G^\circ_{7/2}$			80654.9 2 1239.85		81420.6 8 1228.19		
419							
$^4G^\circ_{5/2}$					81001.2 2 1234.55		81545.4 3 1226.31

in Fig. 2, is here shown in the increasing value of $\Delta\nu$ with increasing atomic number.

Regular Doublet Law

The other doublet law which has already been mentioned, the relativity or regular doublet law in x-ray spectra, serves as another check on the selection of multiplets. This "doublet" must be tested by the $\Delta\nu$ between levels having the same L values but different inner quantum numbers.[17] Landé first noticed that this relation could be applied to optical spectra.[18] Bowen and

Table V. *Mn III. Configuration change* ($3d^44s-3d^44p$).

p \ s	$^4D_{7/2}$	329	$^4D_{5/2}$	242	$^4D_{3/2}$	145	$^4D_{1/2}$
$^4F^\circ_{9/2}$	45818.2 80 2182.54						
167							
$^4F^\circ_{7/2}$	45641.0 30 2190.53		45979.9 70 2174.86				
149							
$^4F^\circ_{5/2}$	45503.9 1 2197.61		45830.4 3 2181.96		46072.5 90 2170.49		
59							
$^4F^\circ_{3/2}$					46013.4 2 2173.28		46158.7 25 2166.44
$^4D^\circ_{7/2}$	51348.9 80 1947.46		51677.4 5 1935.08				
209							
$^4D^\circ_{5/2}$			51468.4 45 1942.94		51707.9 4 1933.94		
168							
$^4D^\circ_{3/2}$					51539.5 30 1940.26		51684.9 1 1934.80
91							
$^4D^\circ_{1/2}$					51450.6 2 1943.61		51593.5 1 1938.23
$^4P^\circ_{5/2}$	42328.76 40 2362.46		42657.93 12 2344.23		42898.39 2 2331.09		
542							
$^4P^\circ_{3/2}$			42113.06 50-x 2374.56		42357.45 50 2360.86		42504.18 8 2357.72
390							
$^4P^\circ_{1/2}$					41967.96 30 2382.77		42113.06 x 2374.56

[17] Sommerfeld, "Atombau" 4th Ed. p. 420.
[18] Landè, Zeits. f. Physik **16**, 394 (1923).

Millikan[13] and Gibbs and White[14] have tested the law for one-electron systems and the latter have applied it to the location of similar multiplets in higher electronic states. One form of this law is

$$\Delta\nu = K(Z - s)^4$$

Table III gives the values of $\nu^{1/4}$ for a few multiplets reported in this investigation. Column 1 gives the configuration, column 2, the levels whose $\Delta\nu$ is used in the calculation and column 6 gives the screening constant. The increase in $\nu^{1/4}$ is nearly linear, but not exactly so in all cases. The introduction of Landé's correction for penetrating orbits does not eliminate the variations from linearity.

TABLE VI. *New term values for V I and Cr II.*

V I.			Cr II		
Referred to $3d^34s^2\ ^4F_{3/2}$			Referred to $3d^5\ ^6S_{5/2}$		
(Russell, Astrophys. J. **66**, 233, 1927)			(C. C. Kiess, Bur. of St. J. of Res. **5**, 775 (1930))		
$3d^44d$	$^6G_{3/2}$	45850.3	$3d^44d$	$^6G_{3/2}$	86571.0
	$^6G_{5/2}$	45883.6		$^6G_{5/2}$	86629.0
	$^6G_{7/2}$	45938.5		$^6G_{7/2}$	86715.7
	$^6G_{9/2}$	46007.1		$^6G_{9/2}$	86827.8
	$^6G_{11/2}$	46085.2		$^6G_{11/2}$	86964.9
	$^6G_{13/2}$	46183.7		$^6G_{13/2}$	87124.2

TABLE VII. *Term values of Mn III, referred to the limit of the sextets, estimated from the Moseley diagram.*

Config.	T.	Value	Config.	T.	Value	Config.	T.	Value
$3d^44d$	$^6F_{11/2}$	111,373	$3d^44p$	$^4D^\circ_{7/2}$	161,172	$3d^44p$	$^6F^\circ_{11/2}$	172,583
		314			209			490
	$^6F_{9/2}$	111,687		$^4D^\circ_{5/2}$	161,381		$^6F^\circ_{9/2}$	173,073
		207			168			400
	$^6F_{7/2}$	111,894		$^4D^\circ_{3/2}$	161,549		$^6F^\circ_{7/2}$	173,473
		151			91			313
	$^6F_{5/2}$	112,045		$^4D^\circ_{1/2}$	161,640		$^6F^\circ_{5/2}$	173,786
		90						224
	$^6F_{3/2}$	112,135		$^4F^\circ_{9/2}$	166,703		$^6F^\circ_{3/2}$	174,010
		52			167			158
	$^6F_{1/2}$	112,187		$^4F^\circ_{7/2}$	166,870		$^6F^\circ_{1/2}$	174,168
					149			
	$^6D_{9/2}$	112,595		$^4F^\circ_{5/2}$	167,019	$3d^44s$	$^4D_{7/2}$	212,521
		207			59			328
	$^6D_{7/2}$	112,802		$^4F^\circ_{3/2}$	167,078		$^4D_{5/2}$	212,849
		160						242
	$^6D_{5/2}$	112,962		$^6D^\circ_{9/2}$	169,684*		$^4D_{3/2}$	213,091
		157		$^4P^\circ_{5/2}$	170,192 *			146
	$^6D_{3/2}$	113,119		$^6D^\circ_{7/2}$	170,467*		$^4D_{1/2}$	213,237
		84		$^6P^\circ_{7/2}$	170,682 *			
	$^6D_{1/2}$	113,203		$^4P^\circ_{3/2}$	170,734 *		$^6D_{9/2}$	220,900
	$^6G_{13/2}$	113,701		$^6D^\circ_{5/2}$	171,103*			298
		317		$^6P^\circ_{5/2}$	171,118 *		$^6D_{7/2}$	221,198
	$^6G_{11/2}$	114,018		$^4P^\circ_{1/2}$	171,124 *			241
		275		$^6P^\circ_{3/2}$	171,466 *		$^6D_{5/2}$	221,439
	$^6G_{9/2}$	114,293		$^6D^\circ_{3/2}$	171,567*			178
		211		$^6D^\circ_{1/2}$	171,855*		$^6D_{3/2}$	221,617
	$^6G_{7/2}$	114,504						132
		102					$^6D_{1/2}$	221,749
	$^6G_{5/2}$	114,606						
		33				$3d^5$	$^6S_{5/2}$	278,552
	$^6G_{3/2}$	114,639						

TABLE VIII. *Term values of Fe IV, referred to the limit of the sextets, estimated from the Moseley diagram.*

Config.	T.	Value	Config.	T.	Value	Config.	T.	Value
$3d^44d$	$^6G_{13/2}$	210,479	$3d^44p$	$^6D^\circ_{9/2}$	283,473*	$3d^44p$	$^6F^\circ_{5/2}$	291,379
		575						388
	$^6G_{11/2}$	211,054		$^4P^\circ_{5/2}$	285,994 *		$^6F^\circ_{3/2}$	291,767
		509						240
	$^6G_{9/2}$	211,563		$^6P^\circ_{7/2}$	286,217 *		$^6F^\circ_{1/2}$	292,007
		417						
	$^6G_{7/2}$	211,980		$^6D^\circ_{7/2}$	286,633*	$3d^44s$	$^4D_{7/2}$	341,056
		247						448
	$^6G_{5/2}$	212,227		$^4P^\circ_{3/2}$	286,639 *		$^4D_{5/2}$	341,504
		88		$^6P^\circ_{5/2}$	286,921 *			308
	$^6G_{3/2}$	212,315		$^4P^\circ_{1/2}$	287,032 *		$^4D_{3/2}$	341,812
								184
$3d^44p$	$^4D^\circ_{7/2}$	273,472		$^6P^\circ_{3/2}$	287,446 *		$^4D_{1/2}$	341,996
		265						
	$^4D^\circ_{5/2}$	273,737		$^6D^\circ_{5/2}$	287,566*		$^6D_{9/2}$	350,464
		143			663			597
	$^4D^\circ_{3/2}$	273,880		$^6D^\circ_{3/2}$	288,231*		$^6D_{7/2}$	351,061
		111			391			476
	$^4D^\circ_{1/2}$	273,991		$^6D^\circ_{1/2}$	288,622*		$^6D_{5/2}$	351,537
				$^6F^\circ_{11/2}$	289,152			342
	$^4F^\circ_{9/2}$	281,584			935		$^6D_{3/2}$	351,879
		246		$^6F^\circ_{9/2}$	290,087			253
	$^4F^\circ_{7/2}$	281,830			736		$^6D_{1/2}$	352,132
		180		$^6F^\circ_{7/2}$	290,823			
	$^4F^\circ_{5/2}$	282,010			556	$3d^5$	$^6S_{5/2}$	460,278
		97						
	$^4F^\circ_{3/2}$	282,107						

TABLE IX. *Term values of Co V referred to the limit of the sextets, estimated from the Moseley diagram.*

Config.	T.	Value	Config.	T.	Value	Config.	T.	Value
$3d^44d$	$^6G_{13/2}$	337,287	$3d^44p$	$^6D^\circ_{9/2}$	431,194*	$3d^44p$	$^6F^\circ_{5/2}$	438,762
		929						573
	$^6G_{11/2}$	338,216		$^6P^\circ_{7/2}$	431,488 *		$^6F^\circ_{3/2}$	439,335
		785						376
	$^6G_{9/2}$	339,001		$^4P^\circ_{5/2}$	431,976 *		$^6F^\circ_{1/2}$	439,711
		631						
	$^6G_{7/2}$	339,632		$^6P^\circ_{5/2}$	432,622 *	$3d^44s$	$^4D_{7/2}$	501,264
		425						626
	$^6G_{5/2}$	340,057		$^4P^\circ_{3/2}$	432,757 *		$^4D_{5/2}$	501,890
		312						428
	$^6G_{3/2}$	340,369		$^6D^\circ_{7/2}$	432,934*		$^4D_{3/2}$	502,318
								265
$3d^44p$	$^4F^\circ_{9/2}$	426,409		$^4P^\circ_{1/2}$	433,306 *		$^4D_{1/2}$	502,583
		274						
	$^4F^\circ_{7/2}$	426,683		$^6P^\circ_{3/2}$	433,437 *		$^6D_{9/2}$	509,796
		197						851
	$^4F^\circ_{5/2}$	426,880		$^6D^\circ_{5/2}$	434,130*		$^6D_{7/2}$	510,647
		145						677
	$^4F^\circ_{3/2}$	427,025		$^6D^\circ_{3/2}$	434,977*		$^6D_{5/2}$	511,324
								524
				$^6D^\circ_{1/2}$	435,463*		$^6D_{3/2}$	511,848
								314
				$^6F^\circ_{11/2}$	435,484		$^6D_{1/2}$	512,162
					1,374			
				$^6F^\circ_{9/2}$	436,858	$3d^5$	$^6S_{5/2}$	673,859
					1,073			
				$^6F^\circ_{7/2}$	437,931			
					831			

Tables of Term Values and Wave-lengths

Two illustrations of multiplet groups of lines are given in Tables IV and V. Each line is represented by its frequency, intensity and wave-length in a vacuum. About fifty lines have been traced for the change in configuration $3d^44s-3d^44p$ through the sequence which starts with V I. Approximately half of these go through to Ni VI, the remainder to Co V. In the other three electronic changes, $3d^44p-3d^44d$, $3d^5-3d^4p$ and $3d^44s^2-3d^34sp$, twenty lines have been traced to Co V, and in addition some fainter multiplet lines found in Mn III. Tables VI, VII, VIII, IX and X give the energy level values referred to the lowest level, $3d^4\ {}^5D_0$ of the corresponding atom which has lost one more electron. These values depend on the limits of the sextets in V I and

Table X. *Term values of Ni VI referred to the limit of the sextets, estimated from the Moseley diagram.*

Config.	T.	Value	Config.	T.	Value	Config.	T.	Value
$3d^44d$	${}^6G_{13/2}$	494,090	$3d^44p$	${}^6F^\circ_{9/2}$	613,691	$3d^44s$	${}^4D_{3/2}$	692,038
		1,286			1,485			373
	${}^6G_{11/2}$	495,376		${}^6F^\circ_{7/2}$	615,176		${}^4D_{1/2}$	692,411
					1,146			
$3d\ 4p$	${}^4F^\circ_{9/2}$	604,140		${}^6F^\circ_{5/2}$	616,322		${}^6D_{9/2}$	698,896
		333			1,045			1,273
	${}^4F^\circ_{7/2}$	604,473		${}^6F^\circ_{3/2}$	617,367		${}^6D_{7/2}$	700,169
		270			507			976
	${}^4F^\circ_{5/2}$	604,743		${}^6F^\circ_{1/2}$	617,874		${}^6D_{5/2}$	701,145
		100						642
	${}^4F^\circ_{3/2}$	604,843	$3d^44s$	${}^4D_{7/2}$	690,561		${}^6D_{3/2}$	701,787
					852			341
	${}^6P^\circ_{7/2}$	606,982		${}^4D_{5/2}$	691,413		${}^6D_{1/2}$	702,128
		1,727			625			
	${}^6P^\circ_{5/2}$	608,709						
		1,154						
	${}^6P^\circ_{3/2}$	609,863						
	${}^6F^\circ_{11/2}$	611,508						
		2,183						

Table XI. *Wave-lengths of new lines.*

Vanadium I

λ(I.A. air)	Int.	ν (vac.)	Origin
			$3d^44p$ $3d^44d$
4799.01	8	20831.9	${}^6F^\circ_{11/2}-{}^6G_{11/2}$
4785.46	1	20890.8	${}^6F^\circ_{7/2}-{}^6G_{5/2}$
4784.48	30-x	20895.1	${}^6F^\circ_{9/2}-{}^6G_{9/2}$
4776.44	60	20930.3	${}^6F^\circ_{11/2}-{}^6G_{13/2}$
4773.06	10	20945.1	${}^6F^\circ_{7/2}-{}^6G_{7/2}$
4766.68	50	20973.1	${}^6F^\circ_{9/2}-{}^6G_{11/2}$
4764.13	4	20984.3	${}^6F^\circ_{5/2}-{}^6G_{5/2}$
4757.48	50	21013.7	${}^6F^\circ_{7/2}-{}^6G_{9/2}$
4756.01	1	21020.2	${}^6F^\circ_{3/2}-{}^6G_{3/2}$
4751.58	35	21039.8	${}^6F^\circ_{5/2}-{}^6G_{7/2}$
4748.51	38	21053.4	${}^6F^\circ_{3/2}-{}^6G_{5/2}$
4746.66	35	21061.6	${}^6F^\circ_{1/2}-{}^6G_{3/2}$

Chromium II

λ (I.A. air)	Int.	ν (vac.)	Origin
			$3d^44p$ $3d^43d$
2558.28	12	39075.3	${}^6F^\circ_{11/2}-{}^6G_{9/2}$
2549.43	40	39211.2	${}^6F^\circ_{11/2}-{}^6G_{11/2}$
2539.76	10	39360.8	${}^6F^\circ_{9/2}-{}^6G_{9/2}$
2539.11	60	39370.8	${}^6F^\circ_{11/2}-{}^6G_{13/2}$
2537.60	12	39392.7	${}^6F^\circ_{7/2}-{}^6G_{5/2}$
2531.79	40	39485.0	${}^6F^\circ_{7/2}-{}^6G_{7/2}$
2530.93	60	39498.4	${}^6F^\circ_{9/2}-{}^6G_{11/2}$
2525.47	8	39583.9	${}^6F^\circ_{5/2}-{}^6G_{5/2}$
2524.52	40	39598.8	${}^6F^\circ_{7/2}-{}^6G_{9/2}$
2520.42	20	39663.3	${}^6F^\circ_{3/2}-{}^6G_{3/2}$
2519.79	40	39673.6	${}^6F^\circ_{5/2}-{}^6G_{7/2}$
2516.70	30	39722.1	${}^6F^\circ_{3/2}-{}^6G_{5/2}$
2515.20	8	39745.8	${}^6F^\circ_{1/2}-{}^6G_{3/2}$

Cr II as calculated by Russell,[14] and the Moseley diagram of Fig. 3. From the most recent values of the constants involved in the relation between principal ionization potential and term value, the ionization potentials were calculated from the equation,

$$V=0.00012336\times\text{term value in cm}^{-1}.$$

In this case "principal ionization potential" is used to designate the potential necessary to remove, completely, one electron, changing the atom from the lowest energy in the state under discussion to the lowest energy in the next

TABLE XII. *Wave-lengths of Mn III, in order of increasing frequency.*

λ(I.A.)	Int.	ν (vac.)	Origin
			$3d^44s$ $3d^44p$
2382.77	30	41967.9	$^4D_{3/2}-{}^4P^\circ_{1/2}$
2374.56	50-x	42113.1	$^4D_{5/2}-{}^4P^\circ_{3/2}$
2362.46	40	42328.8	$^4D_{7/2}-{}^4P^\circ_{5/2}$
2360.86	50	42357.4	$^4D_{3/2}-{}^4P^\circ_{3/2}$
2352.72	8	42504.2	$^4D_{1/2}-{}^4P^\circ_{3/2}$
2344.23	12	42657.9	$^4D_{5/2}-{}^4P^\circ_{5/2}$
2331.09	2	42898.4	$^4D_{3/2}-{}^4P^\circ_{5/2}$
2197.61	1	45503.9	$^4D_{7/2}-{}^4F^\circ_{5/2}$
2190.53	30	45651.0	$^4D_{7/2}-{}^4F^\circ_{7/2}$
2182.54	80	45818.2	$^4D_{7/2}-{}^4F^\circ_{9/2}$
2181.96	3	45830.4	$^4D_{5/2}-{}^4F_5{}^\circ{}_{/2}$
2174.86	70	45979.9	$^4D_{5/2}-{}^4F^\circ_{7/2}$
2173.28	2	46013.4	$^4D_{3/2}-{}^4F^\circ_{3/2}$
2170.49	90	46072 5	$^4D_{3/2}-{}^4F^\circ_{5/2}$
2166.44	28	46158.7	$^4D_{1/2}-{}^4F^\circ_{3/2}$
2009.80	1	49756 2	$^6D_{3/2}-{}^6D^\circ_{1/2}$
2005.27	3	49868.6	$^6D_{5/2}-{}^6D^\circ_{3/2}$
2004.45	2	49889.0	$^6D_{1/2}-{}^6D^\circ_{1/2}$
2001.32	20	49967.0	$^6D_{5/2}-{}^6P^\circ_{3/2}$
1998.16	30	50046 0	$^6D_{3/2}-{}^6D^\circ_{3/2}$
1997.04	25	50074.1	$^6D_{7/2}-{}^6P^\circ_{5/2}$
1996.30	1	50092.7	$^6D_{7/2}-{}^6D^\circ_{5/2}$
1994.19	25	50145.7	$^6D_{3/2}-{}^6P^\circ_{3/2}$
1992.94	5	50177.1	$^6D_{1/2}-{}^6D^\circ_{3/2}$
1991.32	25	50217.9	$^6D_{9/2}-{}^6P^\circ_{7/2}$
1987.57	4	50312.7	$^6D_{5/2}-{}^6P^\circ_{5/2}$
1986.86	30	50330.7	$^6D_{5/2}-{}^6D^\circ_{5/2}$
1982.83	40	50433.0	$^6D_{9/2}-{}^6D^\circ_{7/2}$
1979.78	1	50510.7	$^6D_{7/2}-{}^6P^\circ_{7/2}$
1971.29	40	50728.2	$^6D_{7/2}-{}^6D^\circ_{7/2}$
1962.07	40	50966.6	$^6D_{5/2}-{}^6D^\circ_{7/2}$
1952.52	50	51215.7	$^6D_{9/2}-{}^6D^\circ_{9/2}$
1947.46	80	51348.9	$^4D_{7/2}-{}^4D^\circ_{7/2}$
1943.61	2	51450.6	$^4D_{3/2}-{}^4D^\circ_{1/2}$
1942.94	45	51468.4	$^4D_{5/2}-{}^4D^\circ_{5/2}$
1941.34	40	51510.8	$^6D_{7/2}-{}^6D^\circ_{9/2}$
1940.26	30	51539.5	$^4D_{3/2}-{}^4D^\circ_{3/2}$
1938.23	1	51593.5	$^4D_{1/2}-{}^4D^\circ_{1/2}$
1935.08	5	51677.4	$^4D_{5/2}-{}^4D^\circ_{7/2}$
1934.80	1	51684.9	$^4D_{1/2}-{}^4D^\circ_{3/2}$
1933.94	4	51707·9	$^4D_{5/2}-{}^4D^\circ_{3/2}$
			$3d^34s^2$ $3d^34sp$
1817.60	15	55017.6	$^4F_{9/2}-{}^4G^\circ_{7/2}$
1806.50	18	55355.7	$^4F_{9/2}-{}^4G^\circ_{9/2}$
1798.05	18	55650.2	$^4F_{7/2}-{}^4G^\circ_{7/2}$
1793.57	10	55818.2	$^4F_{5/2}-{}^4G^\circ_{5/2}$
1790.49	50	55850.6	$^4F_{9/2}-{}^4G^\circ_{11/2}$
1786.10	50	55987.9	$^4F_{7/2}-{}^4G^\circ_{9/2}$
1782.19	40	56110.1	$^4F_{5/2}-{}^4G^\circ_{7/2}$
1780.68	6	56158.3	$^4F_{3/2}-{}^4G^\circ_{5/2}$
			$3d^44p$ $3d^43d$
1707.46	35	58566.5	$^6F'_{11/2}-{}^6G^\circ_{11/2}$
1701.12	2	58784.8	$^6F^\circ_{9/2}-{}^6G_{9/2}$
1698.31	35	58882.1	$^6F^\circ_{11/2}-{}^6G_{13/2}$
1695.55	1	58977.9	$^6F^\circ_{7/2}-{}^6G_{7/2}$
1693.22	40	59059.1	$^6F^\circ_{9/2}-{}^6G_{11/2}$
1689.52	15	59188.1	$^6F^\circ_{7/2}-{}^6G_{9/2}$
1686.62	25	59290.2	$^6F^\circ_{5/2}-{}^6G_{7/2}$
1684.10	1	59378.5	$^6F^\circ_{3/2}-{}^6G_{3/2}$
1683.17	20	59411.7	$^6F^\circ_{3/2}-{}^6G_{5/2}$
1679.69	10	59534.8	$^6F^\circ_{1/2}-{}^6G_{3/2}$
1666.99	60	59988.4	$^6F^\circ_{11/2}-{}^6D_{9/2}$
1659.21	25	60269,6	$^6F^\circ_{9/2}-{}^6D_{7/2}$
1653.50	40	60477.8	$^6F^\circ_{9/2}-{}^6D_{9/2}$
1652.66	10	60508.5	$^6F^\circ_{7/2}-{}^6D_{5/2}$
1648.30	15	60668.6	$^6F^\circ_{7/2}-{}^6D_{7/2}$
1644.39	5	60812.8	$^6F^\circ_{3/2}-{}^6D_{1/2}$
1644.05	tr.	60825.4	$^6F^\circ_{5/2}-{}^6D_{5/2}$
1642.72	18	60874.6	$^6F^\circ_{7/2}-{}^6D_{9/2}$
1642.14	1	60896.2	$^6F^\circ_{3/2}-{}^6D_{3/2}$
1640.13	tr	60970.0	$^6F^\circ_{1/2}-{}^6D_{1/2}$
1639.77	10	60984.2	$^6F^\circ_{5/2}-{}^6D_{7/2}$
1633.71	45	61210.4	$^6F_1{}^\circ{}_{1/2}-{}^6F_{11/2}$
1629.15	30	61383.6	$^6F^\circ_{9/2}-{}^6F_{9/2}$
1623.89	25	61580.5	$^6F^\circ_{7/2}-{}^6F_{7/2}$
1619.59	20	61744.0	$^6F^\circ_{5/2}-{}^6F_{5/2}$
1618.46	2	61787.1	$^6F^\circ_{7/2}-{}^6F_{9/2}$
1615.96	10	61882.7	$^6F^\circ_{3/2}-{}^6F_{3/2}$
1615.62	8	61895.7	$^6F^\circ_{5/2}-{}^6F_{7/2}$
1613.63	5	61972.1	$^6F^\circ_{3/2}-{}^6F_{5/2}$
1613.22	1	61987.8	$^6F^\circ_{1/2}-{}^6F_{1/2}$
1611.86	2	62040.1	$^6F^\circ_{1/2}-{}^6F_{3/2}$
			$3d^5$ $3d^44p$
925.2	10	108081.	$^6S_{5/2}-{}^6P^\circ_{3/2}$
922.2	40	108431	$^6S_{5/2}-{}^6P^\circ_{5/2}$
918.5	100	108870	$^6S_{5/2}-{}^6P^\circ_{7/2}$

higher state of ionization. Since $3d^5\ {}^6S$ is the lowest level for Mn III, Fe IV and Co V, the value of this level referred to $3d^4\ {}^5D_0$ of each atom in its next higher state of ionization, was used in the calculation. The results are; Mn III 34.4 volts, Fe IV 56.8 volts and Co V 83.1 volts.

The final tables, XI to XV, give the new lines for this sequence. For each element studied, the values of wave-length, intensity, frequency and origin are given, the order being that of increasing frequency.

The writer wishes to take this opportunity to express her thanks for the use of the vacuum spectrograph and her appreciation of the very helpful advice of Professor R. C. Gibbs during the progress of this investigation.

TABLE XIII. *Wave-lengths of Fe IV in order of increasing frequency.*

λ (I.A.)	Int.	ν (vac.)	Origin
			$3d^44s$ — $3d^44p$
1825.55	8	54778.0	${}^4D_{3/2}-{}^4P^\circ_{1/2}$
1822.72	2	54863.1	${}^4D_{5/2}-{}^4P^\circ_{3/2}$
1819.29	1	54966.5	${}^4D_{1/2}-{}^4P^\circ_{1/2}$
1815.61	25	55061.8	${}^4D_{7/2}-{}^4P^\circ_{5/2}$
1812.53	1	55171.5	${}^4D_{3/2}-{}^4P^\circ_{3/2}$
1801.53	5	55508.4	${}^4D_{5/2}-{}^4P^\circ_{5/2}$
1688.44	2	59226.3	${}^4D_{7/2}-{}^4F^\circ_{7/2}$
1681.45	25	59472.5	${}^4D_{7/2}-{}^4F^\circ_{9/2}$
1680.86	1	59493.4	${}^4D_{5/2}-{}^4F^\circ_{5/2}$
1675.78	25	59673.7	${}^4D_{5/2}-{}^4F^\circ_{7/2}$
1674.89	5	59705.4	${}^4D_{3/2}-{}^4F^\circ_{3/2}$
1672.18	5	59802.2	${}^4D_{3/2}-{}^4F^\circ_{5/2}$
1669.73	2	59889.9	${}^4D_{1/2}-{}^4F^\circ_{3/2}$
1663.52	10	60113.4	${}^6D_{3/2}-{}^6F^\circ_{3/2}$
1663.21	10	60124.7	${}^6D_{1/2}-{}^6F^\circ_{1/2}$
1662.26	20	60159.1	${}^6D_{5/2}-{}^6F^\circ_{5/2}$
1660.07	20	60238.4	${}^6D_{7/2}-{}^6F^\circ_{7/2}$
1656.61	15	60364.2	${}^6D_{1/2}-{}^6F^\circ_{3/2}$
1656.25	10	60377.5	${}^6D_{9/2}-{}^6F^\circ_{9/2}$
1652.85	20	60501.6	${}^6D_{3/2}-{}^6F^\circ_{5/2}$
1647.05	45	60714.6	${}^6D_{5/2}-{}^6F^\circ_{7/2}$
1640.03	65	60974.5	${}^6D_{7/2}-{}^6F^\circ_{9/2}$
1630.99	75	61312.4	${}^6D_{9/2}-{}^6F^\circ_{11/2}$
1579.73	3	63302.0	${}^6D_{5/2}-{}^6D^\circ_{3/2}$
1574.68	8	63505.0	${}^6D_{1/2}-{}^6D^\circ_{1/2}$
1571.21	10	63645.2	${}^6D_{3/2}-{}^6D^\circ_{3/2}$
1566.54	3	63834.9	${}^6D_{9/2}-{}^6D^\circ_{7/2}$
1565.05	2	63895.7	${}^6D_{1/2}-{}^6D^\circ_{3/2}$
1563.30	10	63967.2	${}^6D_{5/2}-{}^6D^\circ_{5/2}$
1560.26	15	64091.8	${}^6D_{5/2}-{}^6P^\circ_{3/2}$
1559.08	15	64140.4	${}^6D_{7/2}-{}^6P^\circ_{5/2}$
1556.48	15	64247.4	${}^6D_{9/2}-{}^6P^\circ_{7/2}$
1555.01	1	64308.2	${}^6D_{3/2}-{}^6D^\circ_{5/2}$
1552.11	15	64428.3	${}^6D_{7/2}-{}^6D^\circ_{7/2}$
1547.58	15	64616.9	${}^6D_{5/2}-{}^6P^\circ_{5/2}$
1546.03	8	64681.6	${}^6D_{1/2}-{}^6P^\circ_{3/2}$
1542.15	15	64844.4	${}^6D_{7/2}-{}^6P^\circ_{7/2}$
1540.77	1	64902.5	${}^6D_{5/2}-{}^6D^\circ_{7/2}$
1538.67	25	64991.1	${}^6D_{9/2}-{}^6D^\circ_{9/2}$
1524.67	15	65587.9	${}^6D_{7/2}-{}^6D^\circ_{9/2}$
			$3d^34s^2$ — $3d^34sp$
1487.35	5	67246.8	${}^4F_{9/2}-{}^4G^\circ_{7/2}$
			$3d^44s$ — $3d^44p$
1485.48	12	67318.3	${}^4D_{7/2}-{}^4D^\circ_{5/2}$
1479.65	38	67583.6	${}^4D_{7/2}-{}^4D^\circ_{7/2}$
			$3d^34s^2$ — $3d^34sp$
1477.69	5	67673.2	${}^4F_{9/2}-{}^4G^\circ_{9/2}$
			$3d^44s$ — $3d^44p$
1475.67	28	67765.8	${}^4D_{5/2}-{}^4D^\circ_{5/2}$
1474.52	2	67818.7	${}^4D_{3/2}-{}^4D^\circ_{1/2}$
1472.13	35	67928.8	${}^4D_{3/2}-{}^4D^\circ_{3/2}$
1470.54	2	68002.2	${}^4D_{1/2}-{}^4D^\circ_{1/2}$
1469.92	20	68030.9	${}^4D_{5/2}-{}^4D^\circ_{7/2}$
1469.04	37-x	68071.7	${}^4D_{3/2}-{}^4D^\circ_{5/2}$
			$3d^34s^2$ — $3d^34sp$
1469.04	x	68071.7	${}^4F_{7/2}-{}^4G^\circ_{7/2}$
			$3d^44s$ — $3d^44p$
1468.11	2	68114.8	${}^4D_{1/2}-{}^4D^\circ_{3/2}$
			$3d^34s^2$ — $3d^34sp$
1464.81	40	68268.2	${}^4F_{9/2}-{}^4G^\circ_{11/2}$
1463.25	4	68341.0	${}^4F_{5/2}-{}^4G^\circ_{5/2}$
1459.92	40	68496.9	${}^4F_{7/2}-{}^4G^\circ_{9/2}$
1455.66	25	68697.4	${}^4F_{5/2}-{}^4G^\circ_{7/2}$
1453.67	15	68791.4	${}^4F_{3/2}-{}^4G^\circ_{5/2}$
			$3d^44p$ — $3d^44d$
1280.43	10	78098.8	${}^6F^\circ_{11/2}-{}^6G_{11/2}$
1273.49	2	78524.4	${}^6F^\circ_{9/2}-{}^6G_{9/2}$
1271.08	15	78673.2	${}^6F^\circ_{11/2}-{}^6G_{13/2}$
1268.40	2	78839.5	${}^6F^\circ_{7/2}-{}^6G_{7/2}$
1265.28	15	79033.9	${}^6F^\circ_{9/2}-{}^6G_{11/2}$
1263.47	15	79147.1	${}^6F^\circ_{5/2}-{}^6G_{5/2}$
1261.72	10	79256.9	${}^6F^\circ_{7/2}-{}^6G_{9/2}$
1259.54	30	79394.1	${}^6F^\circ_{5/2}-{}^6G_{7/2}$
1258.68	2	79448.3	${}^6F^\circ_{3/2}-{}^6G_{3/2}$
1257.29	6	79536.1	${}^6F^\circ_{3/2}-{}^6G_{5/2}$
1254.80	10	79694.0	${}^6F^\circ_{1/2}-{}^6G_{3/2}$
			$3d^5$ — $3d^44p$
587.6	2	172829.	${}^6S_{5/2}-{}^6P^\circ_{3/2}$
576.8	40	173368.	${}^6S_{5/2}-{}^6P^\circ_{5/2}$
574.5	50	174061	${}^6S_{5/2}-{}^6P^\circ_{7/2}$

TABLE XIV. *Wave-lengths of Co V in order of increasing frequency.*

λ(I.A.)	Int.	ν (vac.)	Orign.
			$3d^44s$ $3d^44p$
1488.73	20	67171.4	$^4D_{3/2}-{}^4P^\circ_{1/2}$
1486.02	25	67293.8	$^4D_{5/2}-{}^4P^\circ_{3/2}$
1482.91	20	67435.0	$^4D_{1/2}-{}^4P^\circ_{1/2}$
1482.62	25	67448.2	$^4D_{7/2}-{}^4P^\circ_{5/2}$
1476.65	30	67720.8	$^4D_{3/2}-{}^4P^\circ_{3/2}$
1468.98	35	68074.4	$^4D_{5/2}-{}^4P^\circ_{5/2}$
1459.77	15	68503.9	$^4D_{3/2}-{}^4P^\circ_{5/2}$
1389.11	32	71988.5	$^6D_{5/2}-{}^6F^\circ_{3/2}$
1380.21	10	72452.2	$^6D_{1/2}-{}^6F^\circ_{1/2}$
1379.05	10	72513.7	$^6D_{3/2}-{}^6F^\circ_{5/2}$
1378.12	25	72562.1	$^6D_{5/2}-{}^6F^\circ_{5/2}$
1375.20	30	72716.7	$^6D_{7/2}-{}^6F^\circ_{7/2}$
1373.09	30	72828.4	$^6D_{1/2}-{}^6F^\circ_{3/2}$
1371.01	10	72938.9	$^6D_{9/2}-{}^6F^\circ_{9/2}$
1369.30	4	73030.0	$^4D_{7/2}-{}^4F^\circ_{7/2}$
1368.24	30	73086.6	$^6D_{3\ 2}-{}^6F^\circ_{5/2}$
1364.17	30	73304.6	$^4D_{7/2}-{}^4F^\circ_{9/2}$
1362.46	30	73393.9	$^6D_{5/2}-{}^6F^\circ_{7/2}$
1361.32	20	73458.3	$^4D_{5/2}-{}^4F^\circ_{5/2}$
1357.67	30	73655.6	$^4D_{5/2}-{}^4F^\circ_{7/2}$
1356.09	tr.	73741.9	$^4D_{3/2}-{}^4F^\circ_{3/2}$
1355.20	40	73789.8	$^6D_{7/2}-{}^6F^\circ_{9/2}$
1353.42	15	73886.9	$^4D_{3/2}-{}^4F^\circ_{5/2}$
1351.22	6	74007.2	$^4D_{1/2}-{}^4F^\circ_{1/2}$
1345.67	50	74312.4	$^6D_{9/2}-{}^6F^\circ_{11/2}$
1301.12	35	76856.9	$^6D_{5/2}-{}^6D^\circ_{5/2}$
1295.87	40	77168.2	$^6D_{3/2}-{}^6D^\circ_{5/2}$
1295.55	25	77187.3	$^6D_{7/2}-{}^6D^\circ_{7/2}$
1286.95	28	77703.2	$^6D_{9/2}-{}^6D^\circ_{9/2}$
1284.00	15	77881.6	$^6D_{5/2}-{}^6P^\circ_{3/2}$
1281.63	30	78025.6	$^6D_{7/2}-{}^6P^\circ_{5/2}$
1277.01	50	78307.9	$^6D_{9/2}-{}^6P^\circ_{7/2}$
1275.52	2	78399.4	$^6D_{3/2}-{}^6P^\circ_{3/2}$
1272.23	20	78602.1	$^6D_{11/2}-{}^6D^\circ_{11/2}$
1270.70	20	78696.8	$^6D_{5/2}-{}^6P^\circ_{5/2}$
1270.44	tr.	78712.9	$^6D_{1/2}-{}^6P^\circ_{3/2}$
1263.28	5	79159.0	$^6D_{7/2}-{}^6P^\circ_{7/2}$
1258.61	6	79452.7	$^6D_{9/2}-{}^6D^\circ_{11/2}$
λ(I.A.)	Int.	ν (vac.)	Origin.
			$3d^34s^2$ $3d^34sp$
1246.91	8	80198.2	$^4F_{9/2}-{}^4G^\circ_{9/2}$
1239.85	2	80654.9	$^4F_{7/2}-{}^4G^\circ_{7/2}$
1236.95	20	80844.0	$^4F_{9/2}-{}^4G^\circ_{11/2}$
1234.55	2	81001.2	$^4F_{5/2}-{}^4G^\circ_{5/2}$
1231.73	15	81186.6	$^4F_{7/2}-{}^4G^\circ_{9/2}$
1228.19	8	81420.6	$^4F_{5/2}-{}^4G^\circ_{7/2}$
1226.31	3	81545.4	$^4F_{3/2}-{}^4G^\circ_{5/2}$
			$3d^44p$ $3d^44d$
1028.08	1	97268.7	$^6F^\circ_{11/2}-{}^6G_{11/2}$
1021.14	10	97853.1	$^6F^\circ_{9/2}-{}^6G_{9/2}$
1018.36	10	98197.1	$^6F^\circ_{11/2}-{}^6G_{13/2}$
1017.43	1	98286.9	$^6F^\circ_{7/2}-{}^6G_{7/2}$
1013.80	10	98638.8	$^6F^\circ_{9/2}-{}^6G_{11/2}$
1010.94	10	98917.8	$^6F^\circ_{7/2}-{}^6G_{9/2}$
1009.02	15	99106.1	$^6F^\circ_{5/2}-{}^6G_{7/2}$
1007.51	10	99254.6	$^6F^\circ_{3/2}-{}^6G_{5/2}$
1006.86	4	99318.7	$^6F^\circ_{1/2}-{}^6G_{3/2}$
			$3d^5$ $3d^44p$
415.94	1	240419.	$^6S_{5/2}-{}^6P^\circ_{3/2}$
414.52	5	241243	$^6S_{5/2}-{}^6P^\circ_{5/2}$
412.59	10	242371	$^6S_{5/2}-{}^6P^\circ_{7/2}$

TABLE XV. *Wave-lengths for Ni VI in order of increasing frequency.*

λI.A.	Int.	ν (vac.)	Origin.
			$3d^44s$ $3d^44p$
1191.72	5	83912.3	$^6D_{3/2}-{}^6F^\circ_{1/2}$
1186.90	2	84253.1	$^6D_{1/2}-{}^6F^\circ_{1/2}$
1184.56	4	84419.5	$^6D_{3/2}-{}^6F^\circ_{3/2}$
1179.80	20	84760.2	$^6D_{1/2}-{}^6F^\circ_{3/2}$
1170.08	15	85464.2	$^6D_{3/2}-{}^6F^\circ_{5/2}$
1163.20	10	85969.7	$^6D_{5/2}-{}^6F^\circ_{7/2}$
1161.61	2	86088.2	$^4D_{7/2}-{}^4F^\circ_{7/2}$
1157.13	15	86420.7	$^4D_{7/2}-{}^4F^\circ_{9/2}$
1156.36	12	86478.3	$^6D_{9/2}-{}^6F^\circ_{9/2}$
1153.79	2	86670.9	$^4D_{5/2}-{}^4F^\circ_{5/2}$
1150.22	10	86940.6	$^4D_{5/2}-{}^4F^\circ_{7/2}$
1146.85	8	87195.4	$^4D_{3/2}-{}^4F^\circ_{3/2}$
1145.53	15	87295.8	$^4D_{3/2}-{}^4F^\circ_{5/2}$
λ(I.A.)	Int.	ν (vac.)	Origin.
1144.32	18	87388.1	$^6D_{9/2}-{}^6F^\circ_{11/2}$
1141.96	10	87568.7	$^4D_{1/2}-{}^4F^\circ_{3/2}$
1095.49	8	91283.3	$^6D_{5/2}-{}^6P^\circ_{3/2}$
1093.37	40	91460.4	$^6D_{7/2}-{}^6P^\circ_{5/2}$
1087.97	50	91914.3	$^6D_{9/2}-{}^6P^\circ_{7/2}$
1083.98	5	92252.6	$^6D_{1/2}-{}^6P^\circ_{3/2}$
1081.82	1	92436.8	$^6D_{5/2}-{}^6P^\circ_{5/2}$
1074.51	15	93065.7	$^6D_{3/2}-{}^6P^\circ_{5/2}$
1073.11	12	93187.1	$^6D_{7/2}-{}^6P^\circ_{7/2}$
			$3d^44p$ $3d^44d$
861.09	2	116132	$^6F^\circ_{11/2}-{}^6G_{11/2}$
851.66	20	117418	$^6F^\circ_{11/2}-{}^6G_{13/2}$
844.69	20	118386	$^6F^\circ_{9/2}-{}^6G_{11/2}$