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SPECTRAL RELATIONS BETWEEN CERTAIN ISO-ELECTRONIC SYSTEMS AND SEQUENCES.
PART II; Sc I, Ti II, V III, Cr IV, AND Mn V.

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Abstract

The spectra of doubly ionized vanadium, V III, triply ionized chromium, Cr IV, and quadruply ionized manganese, Mn V.—The neutral atoms of vanadium chromium, and manganese in the normal state contain five valence electrons, $3d^34s^2$, six valence electrons, $3d^54s$, and seven valence electrons, $3d^54s^2$, respectively. The removal of two electrons, $4s^2$, from vanadium, of three electrons, $3d^24s$, from chromium, and of four electrons, $3d^24s^2$, from manganese yields three iso-electronic systems, V III, Cr IV and Mn V, the lowest energy levels of which arise from the three remaining electrons, $3d^3$. The spectra of these three elements so ionized resemble very closely the spectra of neutral scandium and of singly ionized titanium. Extrapolations from the already known data of Sc I, and Ti II, have led to the identification of terms arising from the electron configurations $3d^3$, $3d^24s$, $3d^24p$, and $3d^24d$, for V III, Cr IV and Mn V.

The irregular doublet law.—Following the irregular doublet law the radiated frequencies resulting from transitions between the terms arising from $3d^24p$ and $3d^24s$ as well as combinations between the terms arising from $3d^24d$ and $3d^24p$ in going from element to element are displaced to higher and higher frequencies by very nearly a constant frequency interval. The combination of ordinary energy level diagrams with a Moseley diagram brings out a number of interesting relations between the iso-electronic systems Sc I, Ti II, V III, Cr IV, and Mn V and the two sequences of iso-electronic systems starting with K I and Ca I, respectively. The Moseley diagram and the irregular doublet law are the chief guides in determining approximately the positions of the various doublet and quartet levels as well as the approximate location in the spectrum of the radiated frequencies.

Landé's interval rule and Hund's rule.—The quartet term separations follow fairly well the Landé interval rule, examples of which are given. In general Hund's rule for relative term positions is valid for low lying terms in each spectrum.

Ionization potentials.—The ionization potentials, that is the voltage necessary to remove one $3d$ electron from the normal state $a^4F_2'(3d^3)$ of V III, Cr IV, and Mn V, to the normal state $a^3F_2'(3d^2)$ of the once more ionized atoms, are determined at about 29.6 volts, 50.4 volts, and 75.7 volts respectively.

THE neutral atoms of vanadium, chromium, and manganese in the normal state contain five valence electrons ($3d^34s^2$) six valence electrons ($3d^54s$) and seven valence electrons ($3d^54s^2$) respectively. The removal of two electrons ($4s^2$) from vanadium, of three electrons ($3d^24s$) from chromium, and of four electrons ($3d^24s^2$) from manganese yields three iso-electronic systems V III, Cr IV, and Mn V the lowest energy levels of which arise from the three remaining valence electrons ($3d^3$). The spectra of neutral scandium, Sc I, and of singly ionized titanium, Ti II, have been partially analyzed by a number of investigators.[1] The most complete analysis, how-

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[1] Popow, Ann. d. Physik **45**, 163 (1914); Catalan, An. Soc. Esp. d Fis. y Quim. **21**, 464 (1923); Meggers, Kiess, and Walters, Jour. Opt. Soc. Amer. **9**, 363 (1924).

ever, has been given by Russell and Meggers[2] for Sc I and by Russell[3] for Ti II. Using their data for Sc I and Ti II and extrapolating by means of the *irregular doublet law*, Gibbs and White[4] in a preliminary report were able to identify three quartet multiplets in the spectra of doubly ionized vanadium. With the vacuum spectrograph now available a further study of doubly ionized vanadium has been made and the analysis extended so as to include both triply ionized chromium and quadruply ionized manganese.

Doubly ionized vanadium. The lowest energy levels in the spectrum of V III as already stated arise from the electron configuration $3d^3$. Of the possible nineteen predicted terms ($^2P'$, ^2D, $^2F'$, ^2G, $^2H'$, ^2D, $^4P'$, $^4F'$) arising from three similar d electrons ($3d^3$) all but four have been found. About 45,000 cm^{-1}, above this low set of terms are found the metastable levels $^2F'$ and $^4F'$ of $3d^24s$. Some 42,000 cm^{-1} still higher are found two triads of middle terms $^2D'$, ^2F, $^2G'$, and $^4D'$, ^4F, $^4G'$, arising from $3d^24p$ which combine strongly with the low set of levels of $3d^3$ and the metastable levels of $3d^24s$.

Since the irregular doublet law was so successful in locating the three quartet multiplets[4] arising from transitions between $3d^24p$ and $3d^24s$ it was reasonable to expect that it might prove equally successful in locating the lines arising from the transitions $3d^24d$ to $3d^24p$. Such transitions, however, are known only for Ti II not having yet been found in Sc I, thus making extrapolation difficult. In the previous sequence of iso-electronic systems Ca I to Cr V the transitions $3d\,4p$ to $3d\,4s$, Fig. 3,[5] were displaced successively to the violet by about 11,000 cm^{-1} while the transitions $3d\,4d$ to $3d\,4p$ were displaced successively to the violet by approximately 19,000 cm^{-1}. Since in this sequence of iso-electronic systems, Sc I to Mn V, the transitions $3d^24p$ to $3d^24s$ are displaced successively to the violet by about 12,000 cm^{-1} it was predicted that the transition frequencies $3d^24d$ to $3d^24p$ for V III would lie 20,000 cm^{-1} higher than the corresponding ones in Ti II. This prediction was confirmed by the finding of the $^4G'_{3,4,5,6}-{}^4H'_{4,5,6,7}$, multiplet, in V III, very nearly 20,000 cm^{-1} higher than the corresponding multiplet in Ti II. The term values given in Table VII are computed with respect to $a^4F_2'(3d^3)$ as zero. Term values taken with respect to series limits are given in the fifth and tenth columns of the same table as the square root of the term value, $(\nu)^{1/2}$. All the terms for which $(\nu)^{1/2}$ has been given are taken with respect to the limit $^3F_4'(3d^2)$ of the once more ionized atom. There may be some question as to what limits some of the terms arising from the configuration $3d^3$ approach as it is difficult to associate each term with any series. For convenience only, these terms have been computed with respect to $^3F_4'(3d^2)$ as a limit.

The wave-lengths, frequencies, and intensities of the lines thus far identified in doubly ionized vanadium are given in Table VIII with their corresponding designations.

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[2] Russell and Meggers, Bureau of Standards, Sci. Papers **22**, 329 (1927).

[3] Russell, Astrophys. J. **66**, 283 (1927).

[4] Gibbs and White, Phys. Rev. **29**, 655 (1927).

[5] White, Phys. Rev. **33**, 538 (1929).

Triply ionized chromium. Extrapolating again by means of the irregular doublet law from Sc I, Ti II and V III, to Cr IV two strong doublets and the triad of quartets arising from transitions between the terms $^4D'$, ^4F, $^4G'$, ^2F, $^2G'$ $(3d^24p)$ and the terms $^4F'$, $^2F'(3d^24s)$ have been identified in the spectra of triply ionized chromium about 12,000 cm^{-1} higher than the corresponding doublets and quartets in doubly ionized vanadium. In like manner the multiplet $^4G'_{3,4,5,6}(3d^24p)-{}^4H'_{4,5,6,7}(3d^24d)$ was predicted and identified at very nearly 20,000 cm^{-1} higher than the corresponding multiplet in V III.

TABLE VII. *Term values of doubly ionized vanadium, V III.*

Config. (limit)	Term	Value	Combinations	$(\nu)^{1/2}$
	a^4F_2'	000	$^4G'$, ^4F	
		145	$^4D'$, ^2F	
	a^4F_3'	145	$^2D'$	
		194		
	a^4F_4'	339		
		244		
	a^4F_5'	583		490
	$^2P_1'$	11207	$^2D'$	
		180		
	$^2P_2'$	11387		480
$3d^3$	$^4P_1'$	11513	$^4D'$, ^2F	
		77	$^2D'$	
$(3d^2)$	$^4P_2'$	11590		
		181		
	$^4P_3'$	11771		479
	$^2G_4$	11966	$^4G'$, $^2G'$	
		221	^2F, $^2D'$?	
	$^2G_5$	12187		478
	$^2D_2$	16229	^2F, $^2D'$	
		147		
	$^2D_3$	16376		474
	$^2H_5'$	16822	$^2G'$, ^2F	
		155		
	$^2H_6'$	16977		473
	b^4F_2'	43941	$^4G'$, ^4F	
		167	$^4D'$, ^2F	
	b^4F_3'	44108	$^2D'$	
		236		
$3d^24s$	b^4F_4'	44344		
		301		
$(3d^2)$	b^4F_5'	44645		442
	$^2F_3'$	49329	$^2G'$, ^2F	
		478	$^2D'$	
	$^2F_4'$	49807		437
	$^4G_3'$	85523	a^4F', ^2G	
		351	b^4F', $^2H'$	
	$^4G_4'$	85874		
		431		
	$^4G_5'$	86305		
		503		
	$^4G_6'$	86808		392
	$^4F_2$	86716	a^4F', b^4F'	
		221		
	$^4F_3$	86937		
		281		
	$^4F_4$	87218		
		326		
$3d^24p$	$^4F_5$	87544		391
$(3d^2)$	$^2F_3$	87881	$^2H'$, ^2G	
		448	^2D, a^4F'	
	$^2F_4$	88329	$^2F'$, b^4F' $^4P'$	390
	$^2D_2'$	88560	^2D, $^2P'$	
		386	a^4F', $^4P'$	
	$^2D_3'$	88946	$^2F'$, b^4F'	389
	$^4D_1'$	89004	a^4F', $^4P'$	
		187	b^4F',	
	$^4D_2'$	89191		
		267		
	$^4D_3'$	89458		
		−40		
	$^4D_4'$	89418		388
	$^2G_4'$	91712	$^2H'$, ^2G	
		343	$^2F'$	
	$^2G_5'$	92055		385
	$^4H_4'$	141269	$^4G'$	
		217		
$3d^24d$	$^4H_5'$	141486		
		247		
$(3d^2)$	$^4H_6'$	141733		
		258		
	$^4H_7'$	141991		314

An extrapolation this time on the Moseley diagram of Sc I, Ti II, and V III, predicted the terms arising from $3d^3$, of Cr IV, about 160,000 cm^{-1} lower than the terms arising from $3d^24p$. This predicted the radiated frequen-

TABLE VIII. *Doubly ionized vanadium, V III*

λ vac.	Int.	ν	Designation	Mult. No.	λ vac.	Int.	ν	Designation	Mult. No.
2595.89	170	38522.4	$^2F_4'-{}^2F_4$	1	1378.00	15	72568.9	$^2D_3-{}^2D_3'$	12
2593.84	160	38552.9	$^2F_3'-{}^2F_3$	1	1359.39	1	73562.4	$^2G_4-{}^4G_3'$	13
2564.05	8	39000.8	$^2F_3'-{}^2F_4$	1	1352.99	10	73910.4	$^2G_4-{}^4G_4'$	13
2555.00	160	39138.9	$^2F_4'-{}^2D_3'$	2	1335.09	45	74901.3	$^2H_5'-{}^2G_4'$	14
2548.98	150	39231.4	$^2F_3'-{}^2D_2'$	2	1331.94	50	75078.4	$^2H_6'-{}^2G_5'$	14
2524.16	5	39617.1	$^2F_3'-{}^2D_3'$	2	1329.21	8	75232.6	$^2H_5'-{}^2G_5'$	14
2428.43	2	41178.8	$b^4F_4'-{}^4G_3'$	3	1317.25	20	75915.7	$^2G_4-{}^2F_3$	15
2425.51	2	41228.4	$b^4F_5'-{}^4G_4'$	3	1313.31	30	76143.5	$^2G_5-{}^2F_4$	15
2414.62	40	41414.4	$b^4F_3'-{}^4G_3'$	3	1310.79	1	76289.8	$^4P_2'-{}^2F_3$	16
2407.90	80	41530.0	$b^4F_4'-{}^4G_4'$	3	1309.54	4	76362.7	$^2G_4-{}^2F_4$	15
2404.89	100	41581.9	$b^4F_2'-{}^4G_3'$	3	1306.17	2*d*	76559.7	$^4P_3'-{}^2F_4$	16
2400.40	75	41659.7	$b^4F_5'-{}^4G_5'$	3	1297.90	3	77047.5	$^4P_1'-{}^2D_2'$	18
2394.27	125	41766.4	$b^4F_3'-{}^4G_4'$	3	1295.79	5	77173.0	$^4P_3'-{}^2D_3'$	18
2386.35	10	41905.0	$^2F_4'-{}^2G_4'$	4	1295.79		77173.0	$^2P_2'-{}^2D_2'$	17
2383.18	150	41960.7	$b^4F_4'-{}^4G_5'$	3	1292.77	20	77353.3	$^4P_2'-{}^2D_3'$	18
2371.76	200	42162.8	$b^4F_5'-{}^4G_6'$	3	1292.77		77353.3	$^2P_1'-{}^2D_2'$	17
2366.99	180	42247.7	$^2F_4'-{}^2G_5'$	4	1291.73	4	77415.5	$^4P_2'-{}^4D_1'$	19
2359.42	180	42383.2	$^2F_3'-{}^2G_4'$	4	1291.73		77415.5	$^4P_3'-{}^4D_2'$	19
2348.94	30	42572.4	$b^4F_5'-{}^4F_4$	5	1290.45	10	77492.3	$^4P_1'-{}^4D_1'$	19
2347.78	30	42593.4	$b^4F_4'-{}^4F_3$	5	1289.42	30	77554.2	$^2P_2'-{}^2D_3'$	17
2347.00	30	42607.6	$b^4F_3'-{}^4F_2$	5	1288.64	8	77601.2	$^4P_2'-{}^4D_2'$	19
2337.80	75	42775.1	$b^4F_2'-{}^4F_2$	5	1287.88	20	77647.0	$^4P_3'-{}^4D_4'$	19
2334.87	75	42829.0	$b^4F_3'-{}^4F_3$	5	1287.36	6	77678.3	$^4P_1'-{}^4D_2'$	19
2332.39	75	42874.5	$b^4F_4'-{}^4F_4$	5	1287.23	6	77686.2	$^4P_3'-{}^4D_3'$	19
2331.09	100	42898.4	$b^4F_5'-{}^4F_5$	5	1284.23	15	77867.7	$^4P_2'-{}^4D_3'$	19
2325.78	40	42996.3	$b^4F_2'-{}^4F_3$	5	1257.46	4	79525.4	$^2G_5-{}^2G_4'$	20
2319.65	40	43109.9	$b^4F_3'-{}^4F_4$	5	1253.99	30	79745.4	$^2G_4-{}^2G_4'$	20
2314.81	50	43200.1	$b^4F_4'-{}^4F_5$	5	1252.12	40	79864.6	$^2G_5-{}^2G_5'$	20
2296.89	3	43537.1	$b^4F_4'-{}^2F_3$	6	1248.62	3	80088.4	$^2G_4-{}^2G_5'$	20
2289.21	6	43683.2	$b^4F_5'-{}^2F_4$	6	1172.47	1	85290.0	$a^4F_5'-{}^4G_4'$	21
2275.77	4	43941.2	$b^4F_3'-{}^2F_3$	6	1171.27	4	85377.4	$a^4F_3'-{}^4G_3'$	21
2261.37	2	44221.0	$b^4F_3'-{}^2F_4$	6	1169.28	20	85522.7	$a^4F_2'-{}^4G_3'$	21
2249.60	8	44452.3	$b^4F_3'-{}^2D_2'$	7	1169.11	15	85535.1	$a^4F_4'-{}^4G_4'$	21
2242.08	25	44601.4	$b^4F_4'-{}^2D_3'$	7	1166.58	30	85720.6	$a^4F_5'-{}^4G_5'$	21
2241.13	6	44620.3	$b^4F_2'-{}^2D_2'$	7	1166.47	30	85728.7	$a^4F_3'-{}^4G_4'$	21
2233.46	70	44773.6	$b^4F_5'-{}^4D_4'$	8	1163.27	30	85964.6	$a^4F_4'-{}^4G_5'$	21
2230.24	15	44838.2	$b^4F_3'-{}^2D_3'$	7	1159.77	50	86224.0	$a^4F_5'-{}^4G_6'$	21
2221.93	1	45005.9	$b^4F_2'-{}^2D_3'$	7	1155.12	6	86571.1	$a^4F_3'-{}^4F_2$	22
2219.04	30	45064.5	$b^4F_2'-{}^4D_1'$	8	1154.76	6	86598.1	$a^4F_4'-{}^4F_3$	22
2218.49	25	45075.7	$b^4F_4'-{}^4D_4'$	8	1154.24	70	86637.1	$a^4F_5'-{}^4F_4$	22
2218.09	30	45083.8	$b^4F_3'-{}^4D_2'$	8	1153.19	70	86715.9	$a^4F_2'-{}^4F_2$	22
2216.55	40	45115.2	$b^4F_4'-{}^4D_3'$	8	1152.18	80	86792.0	$a^4F_3'-{}^4F_3$	22
2209.88	8	45251.4	$b^4F_2'-{}^4D_2'$	8	1151.04	90	86877.9	$a^4F_4'-{}^4F_4$	22
2206.96	2	45311.2	$b^4F_3'-{}^4D_4'$	8	1150.26	20	86936.9	$a^4F_2'-{}^4F_3$	22
2205.00	20	45351.5	$b^4F_3'-{}^4D_3'$	8	1149.94	100	86961.0	$a^4F_5'-{}^4F_5$	22
2196.88	2	45519.1	$b^4F_2'-{}^4D_3'$	8	1148.45	10	87073.8	$a^4F_3'-{}^4F_4$	22
1828.89	3	54678.0	$^4G_6'-{}^4H_5'$	9	1146.75	8	87202.9	$a^4F_4'-{}^4F_5$	22
1820.67	7	54924.8	$^4G_6'-{}^4H_6'$	9	1142.36	2	87538.0	$a^4F_4'-{}^2F_3$	23
1812.17	x	(55182.5)	$^4G_5'-{}^4H_5'$	9	1139.82	5	87733.1	$a^4F_3'-{}^2F_3$	23
1812.17	50−x	55182.5	$^4G_6'-{}^4H_7'$	9	1136.57	2	87984.0	$a^4F_4'-{}^2F_4$	23
1805.23	5	55394.6	$^4G_4'-{}^4H_4'$	9	1134.14	6	88172.5	$a^4F_3'-{}^2F_4$	23
1804.12	40	55428.7	$^4G_5'-{}^4H_6'$	9	1131.04	8	88414.2	$a^4F_3'-{}^2D_2'$	24
1798.16	25	55612.4	$^4G_4'-{}^4H_5'$	9	1125.71	30	88832.8	$a^4F_5'-{}^4D_4'$	25
1793.85	20	55746.0	$^4G_3'-{}^4H_4'$	9	1123.55	15	89003.6	$a^4F_2'-{}^4D_1'$	25
1398.47	3	71506.7	$^2D_3-{}^2F_3$	10	1123.00	15	89047.2	$a^4F_3'-{}^4D_2'$	25
1398.44	3	71508.2	$^2H_5'-{}^2F_4$	11	1122.61	12	89078.1	$a^4F_4'-{}^4D_4'$	25
1395.62	1	71652.7	$^2D_2-{}^2F_3$	10	1122.11	15	89117.8	$a^4F_4'-{}^4D_3'$	25
1389.79	20	71953.3	$^2D_3-{}^2F_4$	10	1121.19	8	89190.9	$a^4F_2'-{}^4D_2'$	25
1385.35	2	72183.9	$^2D_3-{}^2D_2'$	12	1119.67	10	89312.0	$a^4F_3'-{}^4D_3'$	25
1382.53	10	72331.1	$^2D_2-{}^2D_2'$	12	1117.84	3?	89458.2	$a^4F_2'-{}^4D_3'$	25

cies arising from transitions between these two sets of terms in the region of 625A. The triad of quartets ${}^4F'(3d^3)-{}^4D'$, ${}^4F$, ${}^4G'(3d^24p)$ have been identified in the region 617A to 636A and the doublets ${}^2G$, ${}^2H'(3d^3)-{}^2F$, ${}^2G'(3d^24p)$ in the region 665A to 695A.

Spectrograms taken in the region of 600A with a vacuum spectrograph in this laboratory have a dispersion of about 11.3A per millimeter. The seventeen lines which constitute the two quartet multiplets $a^4F'-{}^4F$ and $a^4F'-{}^4G'$ lie within the range of 9A, or a little less than one millimeter on the plates. This calls for spectrograms of sharp lines and high resolution which for chromium have been quite difficult to obtain from a vacuum spark. A line marked "tr" in the table of wave-lengths for Cr IV means that only a trace of the line is indicated on the plate, due either to its lying too near a strong line and hence masked or to its being very faint and therefore not accurately measurable. Intercombination lines between doublet and quartet terms in Cr IV seem to be very weak. For this reason the fixing of the doublet term levels with respect to the quartet system of levels by the two lines λλ1791.82 and 1765.15A may be rather questionable.

TABLE IX. *Term values of triply ionized chromium, Cr IV*

Config. (limit)	Term	Value	Combinations	$(\nu)^{1/2}$
	a^4F_2'	000	${}^4D'$, ${}^4F$	
		233		
	a^4F_3'	233	${}^4G'$	
		325		
	a^4F_4'	558		
		391		
$3d^3$	a^4F_5'	949		639
$(3d^2)$	${}^2G_4$	15014	${}^2F$, ${}^2G'$	
		357		
	${}^2G_5$	15371		628
	${}^2H_5'$	21027	${}^2G'$	
		251		
	${}^2H_6'$	21278		623
	b^4F_2'	103989	${}^4D'$, ${}^4F$	
		264		
	b^4F_3'	104253	${}^2F$, ${}^4G'$	
		372		
$3d^24s$	$b\ F_4'$	104625		
		476		
$(3d^2)$	$b\ F_5'$	105101		552
	${}^2F_3'$	109903	${}^2F$, ${}^2G'$	
		760		
	${}^2F_4'$	110663		546
	${}^4G_3'$	157354	a^4F', ${}^4H'$	
		572		
	${}^4G_4'$	157926	b^4F'	
$3d^24p$		696		
	${}^4G_5'$	158622		
$(3d^2)$		821		
	${}^4G_6'$	159443		500
	${}^4F_2$	158519	a^4F'	
		366		
	${}^4F_3$	158885	b^4F'	
		459		
	${}^4F_4$	159344		
		512		
	${}^4F_5$	159856		499
	${}^2F_3$	160265	${}^2F'$, ${}^2G$	
$3d^24p$		642		
	${}^2F_4$	160907	b^4F'	498
$(3d^2)$				
	${}^4D_1'$?	161513	a^4F'	
		321		
	${}^4D_2'$?	161834	b^4F'	
		461		
	${}^4D_3'$	162295		
		−235		
	${}^4D_4'$	162060		497
	${}^2G_4'$	164870	${}^2F'$, ${}^2G$	
		527		
	${}^2G_5'$	165397	${}^2H'$	494
	${}^4H_4'$	233350	G'	
		350		
$3d^24d$	${}^4H_5'$	233700		
		389		
$(3d^2)$	${}^4H_6'$	234089		
		400		
	${}^4H_7'$	234489		418

The term values of Cr IV are given in Table IX with the $^4F_2'$ term taken as zero. The values of $(\nu)^{1/2}$ given in the fifth and tenth columns are taken with respect to the $a^3F_4'(3d)^2$ term of the once more ionized atom in the same way as was done in the case of V III. Wave-lengths, relative intensities, and frequencies of the lines of Cr IV are given in Table X with their corresponding designations.

TABLE X. *Triply ionized chromium, Cr IV*

λ vac.	Int.	ν	Designation	Mult. No.	λ vac.	Int.	ν	Designation	Mult. No.
1990.28	100	50244.2	$^2F_4'-{}^2F_4$	1	1325.08	40	75467.1	$^4G_5'-{}^4H_6'$	7
1985.62	100	50362.1	$^2F_3'-{}^2F_3$	1	1319.71	30	75774.2	$^4G_4'-{}^4H_5'$	7
1960.63	tr	51003	$^2F_3'-{}^2F_4$	1	1315.86	25	75995.9	$^4G_3'-{}^4H_4'$	7
1883.22	35	53100.5	$b^4F_3'-{}^4G_3'$	2	695.19	130	143846	$^2H_5'-{}^2G_4'$	8
1876.15	60	53300.6	$b^4F_4'-{}^4G_4'$	2	693.87	140	144119	$^2H_6'-{}^2G_5'$	8
1873.97	100	53362.6	$b^4F_2'-{}^4G_3'$	2	692.68	12	144367	$^2H_5'-{}^2G_5'$	8
1868.42	45	53521.1	$b^4F_5'-{}^4G_5'$	2	688.46	90	145252	$^2G_4-{}^2F_3$	9
1863.14	125	53672.8	$b^4F_3'-{}^4G_4'$	2	687.12	100	145535	$^2G_5-{}^2F_4$	9
1851.96	150	53996.8	$b^4F_4'-{}^4G_5'$	2	685.44	6	145892	$^2G_4-{}^2F_4$	9
1844.73	6	54208.5	$^2F_4'-{}^2G_4'$	4	668.90	20	149499	$^2G_5-{}^2G_4'$	10
1843.51	15	54244.3	$b^4F_5'-{}^4F_4$	3	667.31	110	149855	$^2G_4'-{}^2G_4'$	10
1843.01	25	54259.0	$b^4F_4'-{}^4F_3$	3	666.55	120	150026	$^2G_5'-{}^2G_5'$	10
1842.77	25	54266.2	$b^4F_3'-{}^4F_2$	3	664.97	6	150383	$^2G_4-{}^2G_5'$	10
1840.20	180	54241.9	$b^4F_5'-{}^4G_6'$	2	636.43	tr	157127	$a^4F_3'-{}^4G_3'$	11
1833.85	40	54530.1	$b^4F_2'-{}^4F_2$	3	635.51	25	157354	$a^4F_2'-{}^4G_3'$	11
1830.44	50	54631.7	$b^4F_3'-{}^4F_3$	3	635.47	0	157364	$a^4F_4'-{}^4G_4'$	11
1827.53	80	54718.7	$b^4F_4'-{}^4F_4$	3	634.22	tr	157674	$a^4F_5'-{}^4G_5'$	11
1827.00	100	54734.5	$^2F_4'-{}^2G_5'$	4	634.12	60	157699	$a^4F_3'-{}^4G_4'$	11
1826.30	100	54755.5	$b^4F_5'-{}^4F_5$	3	632.65	60	158065	$a^4F_4'-{}^4G_5'$	11
1821.62	20	54896.2	$b^4F_2'-{}^4F_3$	3	631.78	15	158283	$a^4F_3'-{}^4F_2$	12
1819.37	90	54964.1	$^2F_3'-{}^2G_4'$	4	631.60	15	158328	$a^4F_4'-{}^4F_3$	12
1815.19	30	55090.6	$b^4F_3'-{}^4F_4$	3	631.33	15	158395	$a^4F_5'-{}^4F_4$	12
1810.56	30	55231.5	$b^4F_4'-{}^4F_5$	3	630.93	100	158496	$a^4F_5'-{}^4G_6'$	11
1791.82	30	55809.2	$b^4F_5'-{}^2F_4$?	5	630.86		158514	$a^4F_2'-{}^4F_2$	12
1765.15	15	56652.4	$b^4F_3'-{}^2F_4$?	5	630.32	90	158650	$a^4F_3'-{}^4F_3$	12
1755.66	60	56958.6	$b^4F_5'-{}^4D_4'$	6		120	158784	$a^4F_4'-{}^4F_4$	12
1741.09	15	57435.3	$b^4F_4'-{}^4D_4'$	6	629.40	40?	158881	$a^4F_2'-{}^4F_3$	12
1738.26	10	57528.8	$b^4F_2'-{}^4D_1'$	6	629.29	150	158909	$a^4F_5'-{}^4F_5$	12
1736.68	20	57581.1	$b^4F_3'-{}^4D_2'$	6	628.52	60	159104	$a^4F_3'-{}^4F_4$	12
1734.07	20	57667.8	$b^4F_4'-{}^4D_3'$	6	627.76	45	159296	$a^4F_4'-{}^4F_5$	12
1729.95	3	57805.1	$b^4F_3'-{}^4D_4'$	6	620.69	100	161111	$a^4F_5'-{}^4D_4'$	13
1728.76	3	57845.0	$b^4F_2'-{}^4D_2'$	6					
1722.94	30	58040.0	$b^4F_3'-{}^4D_3'$	6	619.17	60	161507	$a^4F_4'-{}^4D_4'$	13
1346.60	2	74260.6	$^4G_6'-{}^4H_5'$	7	619.17		161507	$a^4F_2'-{}^4D_1'$	13
1339.65	10	74645.8	$^4G_6'-{}^4H_6'$	7	618.81	60	161600	$a^4F_3'-{}^4D_2'$	13
1338.20	2	74726.7	$^4G_5'-{}^4H_4'$	7	618.27	60	161742	$a^4F_4'-{}^4D_3'$	13
1332.51	50	75046.3	$^4G_6'-{}^4H_7'$	7	617.92	6?	161833	$a^4F_2'-{}^4D_2'$	13
1331.94	10	75077.9	$^4G_5'-{}^4H_5'$	7	617.04	30	162064	$a^4F_3'-{}^4D_3'$	13
1325.83	10	75423.9	$^4G_4'-{}^4H_4'$	7					

Quadruply ionized manganese. Quadruply ionized manganese, Mn V, is the fifth element in the sequence of iso-electronic systems starting with Sc I. The process of extrapolating by use of the irregular doublet law and the Moseley law becomes quite accurate when extended from the radiated frequencies and energy levels of the four preceding elements to the corresponding radiated lines and energy levels of Mn V. As predicted, the transitions between $^4D'$, ^4F, $^4G'$, ^2F, $^2G'(3d^24p)$ and b^4F', $^2F'(3d^24s)$ are found about 12,000 cm^{-1} higher than the corresponding transitions in Cr IV, in the region of $\nu = 66,000$ cm^{-1}, or about $\lambda = 1500$A. The doublet and quartet terms thus identified for $3d^24p$ combine with the lowest terms in the spectrum a^4F', ^2G, $^2H'(3d^3)$ giving lines in the region $\nu = 250,000$ cm^{-1} or about $\lambda = 400$A.

Fortunately the high voltage vacuum spark of manganese gives the sharpest lines that have been obtained from any of the elements in the iron-group. Unfortunately, however, long exposures have failed to bring out Mn V lines very strongly, especially in the short wave-length region of 400 to 500A. For this reason only those lines on the diagonals of the multiplets are readily measured at these short wave-lengths while the lines off the diagonals as well as intercombinations between doublets and quartets in many cases are missing or are very faint and uncertain.

TABLE XI. *Term values of quadruply ionized manganese, Mn V*

Config. (limit)	Term	Value	Combinations	$(\nu)^{1/2}$	Config. (limit)	Term	Value	Combinations	$(\nu)^{1/2}$
	a^4F_2'	000	$^4D,'^4F$			$^4G_3'$	241898	a^4F'	
		333					869		
	a^4F_3'	333	$^4G'$			$^4G_4'$	242767	b^4F'	
		497					1040		
	a^4F_4'	830				$^4G_5'$	243807		
		572					1244		
$3d^3$	a^4F_5'	1402		783		$^4G_6'$	245051		608
$(3d^2)$	$^2G_4$	17852	$^2F, ^2G'$			$^4F_2$	243112	a^4F'	
		556					568		
	$^2G_5$	18408		772	$3d^24p$	$^4F_3$	243680	b^4F'	
	$^2H_5'$	24935	$^2G'$		$(3d^2)$	$^4F_4$	244385		
		426					756		
	$^2H_6'$	25361		767		$^4F_5$	245141		608
	b^4F_2'	176938	$^4D', ^4F$			$^2F_3$	245418	$^2F', ^2G$	
		390					911		
	b^4F_3'	177328	$^4G', ^2F$			$^2F_4$	246329	b^4F'	606
		551							
$3d^24s$	b^4F_4'	177879				$^4D_4'$	247713	a^4F', b^4F'	606
		700							
$(3d^2)$	b^4F_5'	178579		660		$^2G_4'$	250893	$^2F', ^2G$	
							815		
	$^2F_3'$	183466	$^2F, ^2G'$			$^2G_5'$	251708	$^2H'$	601
		1159							
	$^2F_4'$	184625		656					

The two quartet multiplets $a^4F' - {}^4F$, and $a^4F' - {}^4G'$, lie within an interval of 5 A which on the photographic plates cover a little less than 0.5 mm. Manganese in the vacuum spark, however, gives such sharp lines that even the three strongest lines in these two multiplets $\lambda\lambda$410.27, 410.42, and 410.58 A are definitely resolved in spite of their closeness. The outside separation of these three lines on the plates is only 0.028 mm and yet at this short wave-length is equivalent to about 184 wave-numbers. Since small differences in wave-length cause such large differences in radiated frequencies in this region of the spectrum the accuracy of term values and term separations must be greatly impaired.

The term values of Mn V are given in Table XI with the a^4F_2' term taken as zero. The values of $(\nu)^{1/2}$ given in the fifth and tenth columns are taken with respect to the $^3F_4'(3d^2)$ term of the once more ionized atom in the same way as was done in the case of V III and Cr IV. Wave-lengths, relative intensities, and frequencies of the lines thus far identified in Mn V are given in Table XII with their respective designations.

TABLE XII. *Quadruply ionized manganese, Mn V*

λ vac.	Int.	ν	Designation	Mult. No.	λ vac.	Int.	ν	Designation	Mult. No.
1620.65	160	61703.6	$^2F_4'-{}^2F_4$	1	442.56	120	225958	$^2H_5'-{}^2G_4'$	7
1614.16	120	61951.7	$^2F_3'-{}^2F_3$	1	441.80	200	226347	$^2H_6'-{}^2G_5'$	7
1548.70	tr	64570.4	$b^4F_3'-{}^4G_3'$	2	439.43	20	227567	$^2G_4-{}^2F_3$	8
1541.08	60	64889.5	$b^4F_4'-{}^4G_4'$	2	438.75	40	227920	$^2G_5-{}^2F_4$	8
1539.40	80	64960.4	$b^4F_2'-{}^4G_3'$	2	429.11	100	233040	$^2G_4-{}^2G_4'$	9
1533.07	40	65228.6	$b^4F_5'-{}^4G_5'$	2	428.63	100	233301	$^2G_5-{}^2G_5'$	9
1528.13	120	65439.5	$b^4F_3'-{}^4G_4'$	2	413.96	tr	241569	$a^4F_3'-{}^4G_3'$	10
1520.13	tr	65783.8	$b^4F_3'-{}^4F_2$	3	413.39	60	241902	$a^4F_2'-{}^4G_3'$	10
1519.83	40	65796.8	$b^4F_4'-{}^4F_3$	3	413.33		241937	$a^4F_4'-{}^4G_4'$	10
1519.62	40	65805.9	$b^4F_5'-{}^4F_4$	3	412.52	80	242412	$a^4F_5'-{}^4G_5'$	10
1516.78	160	65929.1	$b^4F_4'-{}^4G_5'$	2	412.48		242436	$a^4F_3'-{}^4G_4'$	10
1511.15	40?	66174.7	$b^4F_2'-{}^4F_2$	3	411.89	tr	242783	$a^4F_3'-{}^4F_2$	11
1509.02	4	66268.1	$^2F_4'-{}^2G_4'$	4	411.77	tr	242854	$a^4F_4'-{}^4F_3$	11
1507.11	40	66352.1	$b^4F_3'-{}^4F_3$	3	411.56	120	242978	$a^4F_4'-{}^4G_5'$	10
1504.38	200	66472.6	$b^4F_5-{}^4G_6'$	2	411.56		242978	$a^4F_5'-{}^4F_4$	11
1503.59	80	66507.5	$b^4F_4'-{}^4F_4$	3	411.33	8	243114	$a^4F_2'-{}^4F_2$	11
1502.36	120	66561.9	$b^4F_5'-{}^4F_5$	3	410.93	120	243350	$a^4F_3'-{}^4F_3$	11
1498.30	8	66742.3	$b^4F_2'-{}^4F_3$	3	410.58	160	243558	$a^4F_4'-{}^4F_4$	11
1491.30	30	67055.6	$b^4F_3'-{}^4F_4'$	3	410.42	160	243653	$a^4F_5'-{}^4G_6'$	10
1490.68	160	67083.5	$^2F_4'-{}^2G_5'$	4	410.37	?	243682	$a^4F_2'-{}^4F_3$	11
1486.74	30	67261.2	$b^4F_4'-{}^4F_5$	3	410.27	200	243742	$a^4F_5'-{}^4F_5$	11
1483.09	160	67426.8	$^2F_3'-{}^2G_4'$	4	409.74	30	244057	$a^4F_3'-{}^4F_4$	11
1476.02	30	67749.7	$b^4F_5'-{}^2F_4$	5	409.31	40	244314	$a^4F_4'-{}^4F_5$	11
1446.49	60	69132.9	$b^4F_5'-{}^4D_4'$	6	405.99	120	246311	$a^4F_5'-{}^4D_4'$	12
1431.98	12	69833.4	$b^4F_4'-{}^4D_4'$	6	405.05	60	246883	$a^4F_4'-{}^4D_4'$	12

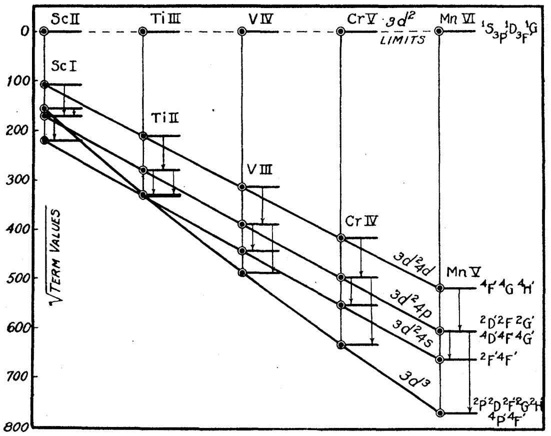

Fig. 5. Energy levels and the Moseley law.

The Moseley diagram law. Combining the data now available for Sc I, and Ti II, and the data here given for V III, Cr IV and Mn V, the same type of *energy-level Moseley diagram* may be drawn for the doublet and quartet terms of these spectra as was drawn for the singlet and triplet terms of the sequence Ca I to Cr V, Fig. 4[5], and for the doublet terms of the sequence K I to V V, Fig. 1[5]. From such a diagram, Fig. 5, two relations similar to those pointed out in Figs. 1[5] and 4[5] are at once recognized; first, the *increased binding of a 3d electron over a 4p and a 4s electron* and second, the *parallelism between the lines $3d^24s$, $3d^24p$, and $3d^24d$.* The singlet and triplet term limits of all the terms are the low ^1S, $^3P'$, ^1D, $^3F'$, ^1G ($3d^2$) terms of the once more ionized atoms as shown at the top of the figure. Although for each electron configuration, including that of the limit, a point has been plotted for the term involving the largest R, L, and J values the points for all the terms in each configuration would lie within the range covered by the circle. A single line has been drawn to represent each set of energy levels and a single arrow to represent all of the observed radiated frequencies resulting from jumps between two sets of energy levels. In order to show the relative shifting of the various terms of any one configuration in going from one iso-electronic system to the next, Fig. 6 has been plotted. Each set of energy levels has been plotted with reference to the horizontal dotted line through the center of the figure. This line of reference is chosen arbitrarily for each set of levels as a weighted mean, each term being weighted in proportion

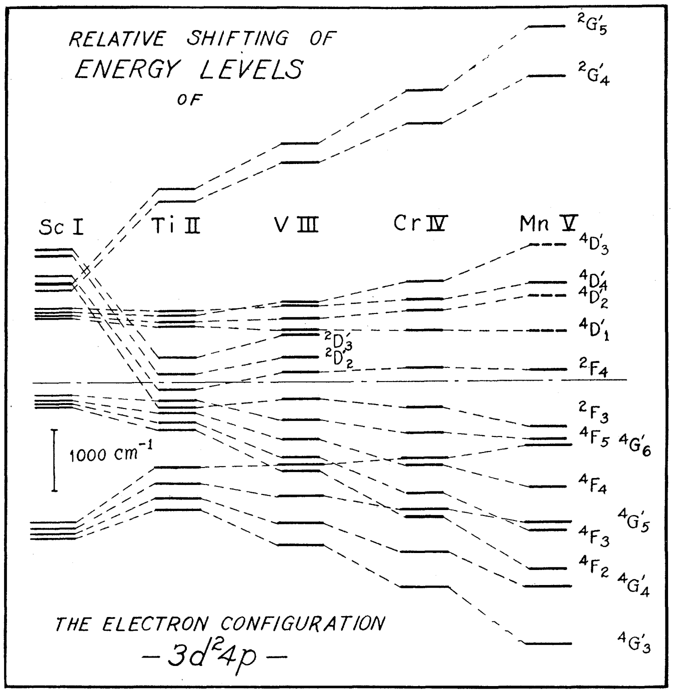

Fig. 6. Relative shifting of energy levels.

to its J value. Since only the ${}^4D_4'$ term has been found for Mn V the other three terms ${}^4D'_{1,2,3}$, may be predicted as shown in the figure by dotted lines. All of these levels in Fig. 6 are represented by but a single line, the line $3d^24p$, in Fig. 5.

TABLE XIII. *Irregular doublet law.*

	$3d^24p$ to $3d^24s$				$3d^24d$ to $3d^24p$	
	${}^4F_5'-{}^4G_6'$	$\Delta\nu$	${}^2F_4'-{}^2G_5'$	$\Delta\nu$	${}^4G_6'-{}^4H_7'$	$\Delta\nu$
Sc I	17626		18109		(15548)	
		12221		11742		(19800)
Ti II	29847		29851		35348	
		12316		12397		19834
V III	42163		42248		55182	
		12219		12486		19864
Cr IV	54342		54734		75046	
		12131		12349		(19900)
Mn V	66473		67083		(94946)	

The irregular doublet law. As has already been indicated two sets of radiated frequencies have been found which follow very closely the *irregular doublet law* first, the set of lines arising from the electron transition $3d^24p$ to $3d^24s$ and second, the set of lines arising from the electron transition $3d^24d$ to $3d^24p$. Examples of this linear relation are given in Table XIII for the lines ${}^4F_5'-{}^4G_6'$ and ${}^2F_4'-{}^2G_5'$ representing the first set of transitions and for the lines ${}^4G_6'-{}^4H_7'$ representing the second set of transitions. None of the terms arising from the electron configuration $3d^24d$ has as yet been determined for Sc I. An extrapolation by means of the last column of Table XIII, however, would locate the frequency of the ${}^4G_6'-{}^4H_7'$ transition not far

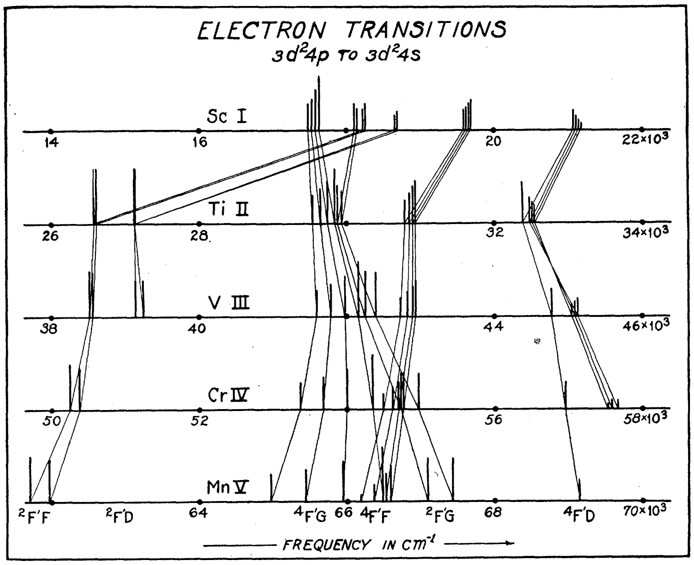

Fig. 7. Regular displacement of frequencies.

from $\nu = 15{,}548$ cm^{-1}. This same multiplet $^4G'H'$, although quite accurately predicted for Mn V, has not been identified with certainty and is therefore not given in the other tables. It is even very weak in Cr IV.

The relative shifting to higher and higher frequencies by very nearly a constant frequency interval of the two triads $^2F'D'$, $^2F'F$, $^2F'G$, and $^4F'D'$, $^4F'F$, $^4F'G'$ $(3d^24s-3d^2dp)$ is shown in Fig. 7. Each frequency scale, although the same for all five elements, has been displaced to the left of the one just preceding it by 12,000 cm^{-1}. A comparison of this figure with the corresponding figure for the two triads ^1DP, $^1DD'$, ^1DF, and ^3DP, $^3DD'$, ^3DF $(3d4s-3d4p)$, Fig. 3[5], of the once more ionized atoms reveals several interesting similarities. For example the more nearly exact linear relation for certain lines starts with the first element in the sequence while for other lines it starts with the second element.

Term separation; The Landé interval rule; and Hund's rule. The systematic increase in term separations in going from one element to the next for each of the four electron configurations $3d^3$, $3d^24s$, $3d^24p$, and $3d^24d$ is shown in Table XIV. In the lower half of the table it is seen that the *Landé interval rule* for quartet terms is followed. This is especially true for the $^4F'_{2,3,4,5}$ terms of $(3d^24s)$ where the observed interval ratios for all five elements are in exact agreement with those predicted by theory.

TABLE XIV. *Quartet term separations and the Landé interval rule.*

	$3d^3$			$3d^24s$			$3d^24p$			$3d^24d$		
	$^4F_2'$ $^4F_3'$ $^4F_4'$ $^4F_5'$			$^4F_2'$ $^4F_3'$ $^4F_4'$ $^4F_5'$			$^4G_3'$ $^4G_4'$ $^4G_5'$ $^4G_6'$			$^4H_4'$ $^4H_5'$ $^4H_6'$ $^4H_7'$		
Sc I	35	48	60	38	52	67	73	94	114			
Ti II	76	103	128	94	131	168	190	234	273	123	138	143
V III	145	194	244	167	236	301	351	431	503	217	247	258
Cr IV	233	325	391	264	372	476	572	696	821	350	389	400
Mn V	333	497	572	390	551	700	869	1040	1244			
Theor.	**2.5**	**3.5**	**4.5**	**2.5**	**3.5**	**4.5**	**3.5**	**4.5**	**5.5**	**4.5**	**5.5**	**6.5**
Sc I	2.6	3.6	4.5	2.5	3.5	4.5	3.5	4.5	5.5			
Ti II	2.7	3.6	4.5	2.5	3.5	4.5	3.8	4.7	5.5	5.6	6.3	6.5
V III	2.7	3.6	4.5	2.5	3.5	4.5	3.8	4.7	5.5	5.5	6.2	6.5
Cr IV	2.7	3.7	4.5	2.5	3.5	4.5	3.8	4.5	5.5	5.7	6.3	6.5
Mn V	2.6	3.9	4.5	2.5	3.5	4.5	3.8	4.6	5.5			

Doublet Term Separations

	$3d^3$ $^2G_4$ $^2G_5$	$3d^24s$ $^2F_3'$ $^2F_4'$	$3d^24p$ $^2F_3$ $^2F_4$	$3d^24p$ $^2G_4'$ $^2G_5'$
Sc I		116	125	95
Ti II	121	269	283	205
V III	221	478	448	343
Cr IV	357	758	642	527
Mn V	556	1159	911	815

Hund's theory gives a satisfactory account of the terms thus far identified. The prediction that from each electron configuration the terms with highest multiplicity, R, and highest L values should lie deepest is verified in all three elements as can be seen from the tables of term values. All of the terms thus far determined for V III, Cr IV, and Mn V are given in Table XV. From this table it is apparent that out of all the theoretically predicted terms comparatively few have so far been identified. There is little doubt, however, that the rest of the terms exist in each of the spectra. By analogy with singly ionized titanium where nearly all the predicted terms have been identified, many of them from weak lines, combinations between the remaining terms for the rest of the elements of the sequence will in general be so weak that one could hope to observe these lines only by making extremely long exposures. The terms given in Table XV do involve nearly all of the strong lines in each spectrum and at the same time include the lowest terms arising from each of the four electron configurations $3d^3$, $3d^24s$, $3d^24p$, and $3d^24d$.

TABLE XV. *Predicted and observed terms.*

Electron Config.	Theoretical Terms	Observed Terms V III	 Cr IV	 Mn V
$3d^3$	$^4P,\ ^4F$ $^2F,\ ^2G,\ ^2H$ $^2P,\ ^2D,\ ^2D$	$^4P',\ a^4F'$ $^2G,\ ^2H'$ $^2P',\ ^2D$	a^4F' $^2G,\ ^2H'$	a^4F' $^2G,\ ^2H'$
$3d^24s$	$^4P,\ ^4F$ $^2S,\ ^2P,\ ^2D$ $^2F,\ ^2G$	b^4F' $^2F'$	b^4F' $^2F'$	b^4F' $^2F'$
$3d^24p$	$^4D,\ ^4F,\ ^4G$ $^2D,\ ^2F,\ ^2G$ $^2F,\ ^2G,\ ^2H$ $^4S,\ ^4P,\ ^4D$ $^2S,\ ^2P,\ ^2D$ $^2S,\ ^2P,\ ^2D$ ^2P	$^4D',\ ^4F,\ ^4G'$ $^2D',\ ^2F,\ ^2G'$	$^4D',\ ^4F\ \ ^4G'$ $^2F,\ ^2G'$	$^4D',\ ^4F,\ ^4G'$ $^2F,\ ^2G'$
$3d^24d$	$^4P,\ ^4D,\ ^4F,\ ^4G,\ ^4H$ $^2P,\ ^2D,\ ^2F,\ ^2G,\ ^2H$ $^2D,\ ^2F,\ ^2G,\ ^2H,\ ^2I$ $^2S,\ ^2P,\ ^2D,\ ^2F,\ ^2G$ $^4P,\ ^4D,\ ^4F$ $^2P,\ ^2D,\ ^2F$ ^2D	$^4H'$	$^4H'$	$^4H'$?

The ionization potentials, that is the voltage necessary to remove one $3d$ electron from the normal state $a^4F_2'(3d^3)$ of V III, Cr IV, and Mn V, to the normal state $a^3F_2'(3d^2)$ of the once more ionized atoms are determined at about 29.6 volts, 50.4 volts, and 75.7 volts respectively.

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