

Cadmium was present in nearly every zinc and brass sample. The lines of cadmium which have been well observed previously have somewhat greater wave-length in the present table. The red line is only slightly increased in wave-length by the powerful source, but the effect on the blue lines, which are multiple, was considerably greater.

The beryllium line lacks sharpness; this may be due to electric effect or to the presence of hyperfine structure.

The wave-lengths of the alkalis are center of gravity values excepting in the case of rubidium 7800A. The reported wave-length of this complex line probably refers to one component. The line is very easily self-reversed, it shows a wide hyperfine structure, and no doubt the isotope separation is measurable. The line occurred as a weak impurity because of the previous use of the lamp house in observing rubidium. The most suitable interferometer separations for resolving 7800A were not sought as the line was not on the present program.

Rods of German silver were used as electrodes

in making a few exposures; these exposures showed several lines of nickel. The nickel lines agree well with the solar wave-lengths of St. John and others,¹ and there seems to be no need to report these values which for the most part rest on a single observation of each line.

In the column headed "p. e." an A means that an accuracy of a part in two million has been obtained; B indicates a part in a million; C shows that the error may be greater than a part in a million; and D indicates that the value is unreliable. In the short wave region, the prism and grating measurements are by Buins; the interferometer measurements are by Boreman, who also observed the beryllium line. The longer region was observed and measured by Hetzler. We are indebted to the Carnegie Institute of Technology and to Dr. F. M. Walters, Jr., for the use of a Hilger E-1 spectroscope, and for assistance in observing. The short wave grating plates were taken at the U. S. Bureau of Standards, by courtesy of Dr. W. F. Meggers, and the late Director G. K. Burgess, Allegheny Observatory, April, 1935.

OCTOBER 15, 1935

PHYSICAL REVIEW

VOLUME 48

Deepest Terms in Ions of the Isoelectronic Sequence A I-Mn VIII

P. GERALD KRUGER AND S. G. WEISSBERG, *Department of Physics, University of Illinois*

(Received July 23, 1935)

Radiations corresponding to the energy differences between the terms $3p^6\ ^1S_0-3p^5\ 4s\ ^3P_1^0, ^1P_1^0$ in Ti V, V VI, Cr VII, Mn VIII and $3p^6\ ^1S_0-3p^5\ 5s\ ^3P_1^0, ^1P_1^0$ in V VI and Cr VII have been observed. These radiations connect the upper states with the deepest terms in each ion and therefore enable the calculation of the ionization potentials. The identification of the lines was facilitated by the use of constant second difference displaced frequency diagrams.

IN a previous report¹ an estimate was given of the absolute value of the ground term $3p^6\ ^1S_0$ of the argon-like ions Sc IV, Ti V, V VI, Cr VII and Mn VIII. The estimate was based on an almost linear extrapolation of the Moseley diagram for the $3p^5\ 4s\ ^1P_1^0$ terms of A I, K II and

The limits of the $3p^6\ ^1S_0-3p^5\ ms\ ^3P_1^0, ^1P_1^0$ series have been calculated for V VI and Cr VII, and have an estimated error in the value of the deepest terms of 0.5 percent. The values of the deepest terms of V VI and Cr VII, calculated from series limits, make possible the calculation of the absolute value of the deepest terms of Sc IV, Ti V and Mn VIII from a Moseley diagram.

Ca III.² It was made by adding the radiation corresponding to the transition $^1S_0-^1P_1^0$ to the extrapolated value of the $^1P_1^0$ term which was obtained from the Moseley diagram. Since then, radiations corresponding to the transitions $3p^6\ ^1S_0-3p^5\ 5s\ ^1P_1^0$ and $3p^6\ ^1S_0-3p^5\ 5s\ ^3P_1^0$ have been observed in V VI and Cr VII. The discovery of

¹ P. G. Kruger and S. G. Weissberg, *Phys. Rev.* **46**, 336 (1934).

² Data from Bacher and Goudsmit, *Atomic Energy States*.

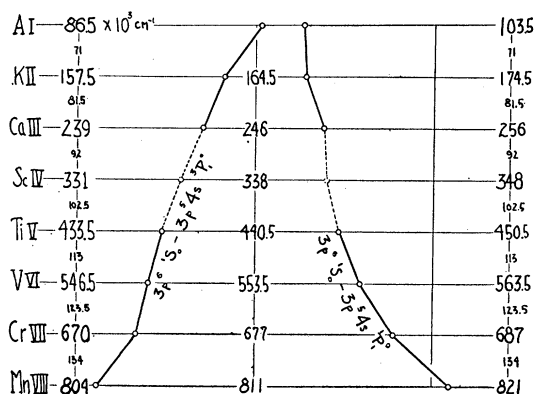


FIG. 1. First series members $3p^6 1S_0 - 3p^5 4s^3 P_1^0, 1P_1$; constant second difference $10,500 \text{ cm}^{-1}$.

the second members of the $1S_0 - ms^1 P_1^0$ and $1S_0 - ms^3 P_1^0$ series enables one to make a calculation of the series limits by use of the Rydberg tables.

All spectrograms were taken with a 21-foot grazing incidence vacuum spectrograph, which has been described previously.^{3,4} The only change in the apparatus was the substitution of three specially constructed General Electric Company 0.3-microfarad pyranol capacitors, in series, for the bank of oil-immersed glass plate

³ P. G. Kruger, Rev. Sci. Inst. 4, 128 (1933).

⁴ P. G. Kruger and W. E. Shoupp, Phys. Rev. 46, 124 (1934).

capacitors used heretofore. As a result, more intense spectra were obtained for a given exposure time than had been obtained with the glass plate capacitors. The intensity for a given exposure time was also augmented by charging and discharging the capacitors three times a second instead of twice a second. To obtain the first members of the series the necessary exposure times were: Ti, 4 hr., V, 4 hr., Cr, 3 hr., and Mn, 4 hr. The second members in V and in Cr were obtained after 5-hr. exposures. The second members in Mn VIII and possibly the third members in Cr VII appeared after 5-hr. exposures, but the wave-lengths are not reported here because the lines occur in a region in which there are not sufficient standards for accurate measurement. ($\lambda \cong 86\text{Å}$ for the Mn VIII lines and $\lambda \cong 94\text{Å}$ for the Cr VII lines.)

When the spectra of Ti, Cr and Mn were photographed, the positive electrode was a cylindrical copper shell in which a piece of pure metal in the form of a hemisphere was mounted. The V electrodes were prepared by heating V_2O_5 powder in a copper shell to red heat in a reducing flame. Since the spectrograms obtained from this electrode showed both V and O lines it was necessary to compare these spectrograms with oxygen spectrograms previously taken in order to obtain a list of lines due to vanadium alone.

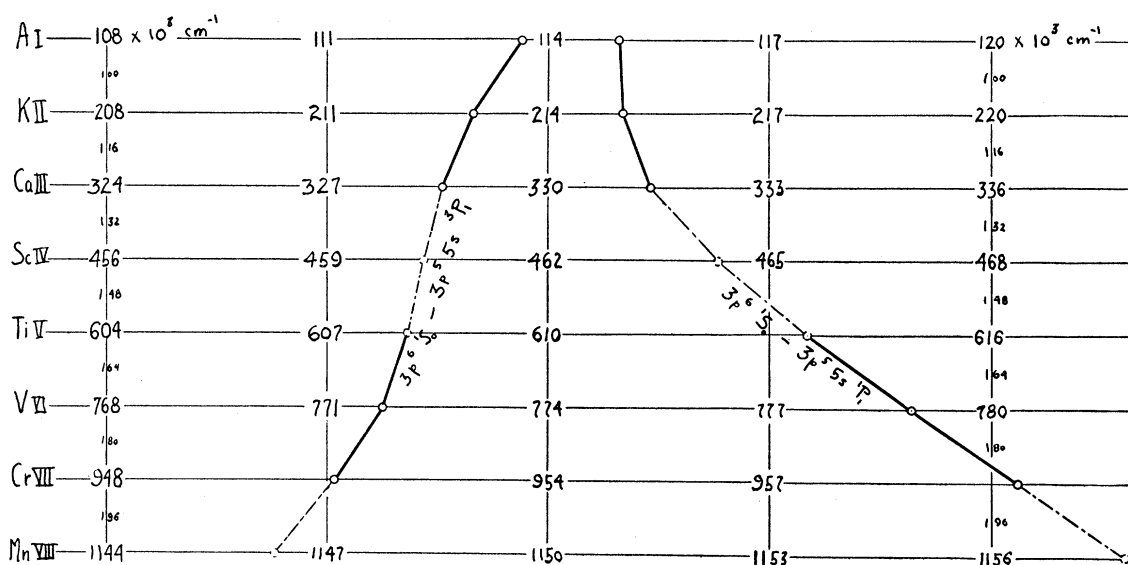


FIG. 2. Second series members $3p^6 1S_0 - 3p^5 5s^3 P_1, 1P_1$; constant second difference $16,000 \text{ cm}^{-1}$.

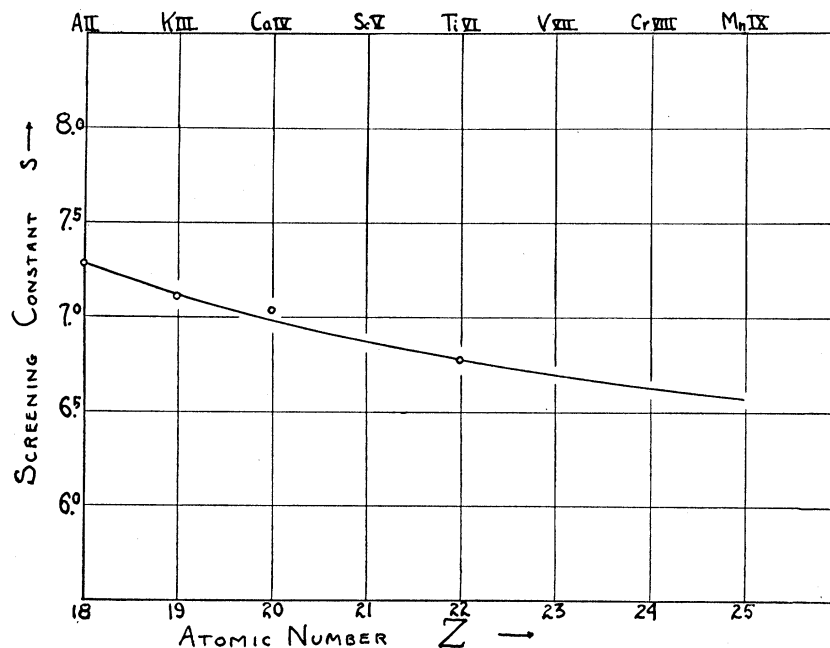


FIG. 3.

A pure copper rod served as the negative electrode in every case.

The method of constant second difference displacement curves,⁴ as shown in Figs. 1 and 2 and in Tables VI and VII was used to predict the approximate wave-lengths of the lines sought. The identifications are unambiguous, inasmuch as the lines are relatively isolated and the dispersion very large. In all cases except the second series members in V VI and Cr VII the strongest lines in the region satisfied the condition that the line of longer wave-length (the intercombination line) was the less intense. Moreover, in the course of following the displacement curves through a sequence, the extrapolated values in no case differed by more than 800 frequency units from the observed values. This corresponds to 0.1Å at 125Å and to 0.3Å at 200Å. The only case in which several lines occurred sufficiently near each other to raise a question of the identification was in the case of Mn VIII. In this case, the two lines picked were the strongest lines in the region, and the more intense line was of shorter wave-length. In the second members of the series in V VI and Cr VII, the line positions were equally unambiguous, but the line of shorter wave-length was the less intense. This apparently anomalous intensity relationship may be com-

pared with the intensity relationship in the corresponding series of Kr I⁵ and Xe I.⁶ In these atoms the $^1S_0-^3P_1^0$ transition is more intense than the $^1S_0-^1P_1^0$, and the coupling tends toward the *jj* type. It is logical to suppose that the coupling in the argon-like ions tends toward *jj* as the principal quantum number increases since the $^1P_1^0$ and $^3P_0^0$ terms approach the $^2P_{1/2}$ state of the chlorine-like ions, while the $^3P_1^0$ and $^3P_2^0$ approach the $^2P_{3/2}$ state of the chlorine-like ions. Thus it may be expected that the second members of the series will have the intensities reversed.

In Table I are listed the wave-lengths, wave

TABLE I. Observed lines and transitions.

ION	RELATIVE INTENSITIES	$\lambda(\text{Å})$	$\nu(\text{cm}^{-1})$	TRANSITIONS
Ti V	75	228.898	436876	$3p^6 1S_0-3p^5 4s 3P_1^0$
	100	225.337	443780	$3p^6 1S_0-3p^5 4s 1P_1^0$
V VI	15	182.050	549300	$3p^6 1S_0-3p^5 4s 3P_1^0$
	20	179.323	557653	$3p^6 1S_0-3p^5 4s 1P_1^0$
	4	129.574	771759	$3p^6 1S_0-3p^5 5s 3P_1^0$
Cr VII	2	128.382	778925	$3p^6 1S_0-3p^5 5s 1P_1^0$
	15	148.736	672332	$3p^6 1S_0-3p^5 4s 3P_1^0$
	25	146.532	682444	$3p^6 1S_0-3p^5 4s 1P_1^0$
	4	105.14	951110	$3p^6 1S_0-3p^5 5s 3P_1^0$
Mn VIII	1.5	104.13	960340	$3p^6 1S_0-3p^5 5s 1P_1^0$
	10	124.254	804803	$3p^6 1S_0-3p^5 4s 3P_1^0$
	15	122.135	818766	$3p^6 1S_0-3p^5 4s 1P_1^0$

⁵ W. F. Meggers, T. L. de Bruin and C. J. Humphreys, Bur. Standards J. Research 3, 129 (1929).

⁶ W. F. Meggers, T. L. de Bruin and C. J. Humphreys, Bur. Standards J. Research 3, 731 (1929).

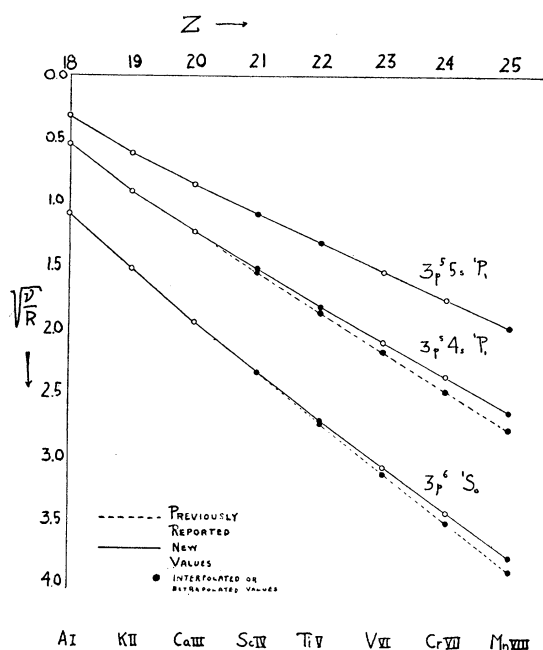


FIG. 4. Moseley diagram.

numbers, and relative intensities of the observed lines, together with the corresponding transitions. For all lines except the two Cr VII lines of shortest wave-length, a linear interpolation between very near Cu secondary standard⁷ lines and a correction curve were used to determine the wave-lengths. The Cr VII lines $\lambda 105.14\text{A}$ and 104.13A were calculated by the use of a quadratic formula,⁷ using two Be lines $\lambda 100.254\text{A}$ and 88.374A ⁸ and the Cu line $\lambda 109.215\text{A}$ as standards. Since there were no other standards in this region it was impossible

TABLE II. Correlation of series limits.

ION	$L(^1P_1^0)$ (cm^{-1})	$L(^3P_1^0)$ (cm^{-1})	1S_0 (ref. 1) (cm^{-1})	$L(^1P_1^0) - L(^3P_1^0)$ (cm^{-1})	$\Delta^2P_{3/2, 1/2}$ (cm^{-1})
A I	128854	127398	127103.8	1456	1431 ^a
K II	258234	256776	256637	1458	2164 ^a
Ca III	415568	413267	413127	2301	3056 ^c
Sc IV	(602400) ^d	(598800) ^d	602000	(3600) ^d	(4300) ^b
Ti V	(812500) ^d	(807700) ^d	824000	(4800) ^d	5828 ^c
V VI	1046420	1040090	1076000	6330	(7600) ^b
Cr VII	1308280	1299700	1359000	8580	(9800) ^b
Mn VIII	(1585000) ^d	(1578000) ^d	1672000	(11000) ^d	(12500) ^b

^a Data from Bacher and Goudsmit, *Atomic Energy States*.

^b From screening constants. See Fig. 3.

^c S. G. Weissberg and P. G. Kruger, *Phys. Rev.* **47**, 798 (1935).

^d Estimated from Moseley diagrams similar to Fig. 4.

⁷ P. G. Kruger and F. S. Cooper, *Phys. Rev.* **44**, 826 (1933).

⁸ P. G. Kruger and F. S. Cooper, *Phys. Rev.* **44**, 418 (1933).

TABLE III. Series limits in rare gas-like ions.

ION	$L(^3P_1^0)$ FROM 2 MEMBERS (cm^{-1})	1S_0 (cm^{-1})	PERCENT DIFF.
Ne I	174312	173930	+0.22
Na II	382795	381528	+0.33
Mg III	648608	646364	+0.34
Al IV	971075	967783	+0.34
Si V	1346639	1342900	+0.27
A I	127397	127103	+0.23
Kr I	113559	112914	+0.57
Rb II	221804	221852	-0.025
Xe I	96335	97835	-1.5

TABLE IV. Ionization potentials.

ION	IONIZATION POTENTIAL (volts)	FIRST DIFFERENCE (volts)	SECOND DIFFERENCE (volts)
A I	15.69		
K II	31.67	15.98	
Ca III	51.0	19.3	3.3
Sc IV	74.0	23.0	3.7
Ti V	99.7	25.7	2.7
V VI	128.4	28.7	3.0
Cr VII	160.4	32.0	2.7
Mn VIII	195.	34.6	2.6

TABLE V. Term values.

ION	$3p^6 1S_0$ (cm^{-1})	$3p^5 4s 3P_1^0$ (cm^{-1})	$3p^5 4s 1P_1^0$ (cm^{-1})	$3p^5 5s 3P_1^0$ (cm^{-1})	$3p^5 5s 1P_1^0$ (cm^{-1})
A I	127103.8	33360.86	31711.62	13468.4	12138.4
K II	256637.	93400.	90176.	43644.	41618.
Ca III	413127.	169200.	165434.	84547.	81729.
Sc IV	(598800)	(268100)	(251200)	(134000)	(129700)
Ti V	(807700)	(370824)	(363920)	(196300)	(189000)
V VI	1040090	490790	482437	268331	261165
Cr VII	1299700	627368	617256	348590	338360
Mn VIII	(1578000)	(771200)	(757200)	(444500)	(428000)

Values in parentheses are estimated from Moseley diagrams of Fig. 4.

TABLE VI. Radiated frequencies with first and second differences (in cm^{-1}). First series members.

IONS	$3p^6 1S_0 - 3p^5 4s 3P_1^0$	$3p^6 1S_0 - 3p^5 4s 1P_1^0$
A I	93742.9	95392
K II	163237	69494
Ca III	243927	80690
Sc IV	(335000)	(91073)
Ti V	436876	(101876)
V VI	549300	112424
Cr VII	672332	123032
Mn VIII	804803	132471
		11196
		166462
		81231
		247693
		(10383)
		(10803)
		(10548)
		443780
		(103780)
		(113873)
		557653
		113873
		124792
		10608
		682445
		9439
		818766
		11070
		81231
		(11076)
		(92307)
		(11473)
		(10093)
		10919
		124792
		11529
		136321

TABLE VII. Radiated frequencies with first and second differences (in cm^{-1}). Second series members.

IONS	$3p^6\ ^1S_0 - 3p^5\ 5s\ ^3P_1^0$			$3p^6\ ^1S_0 - 3p^5\ 5s\ ^1P_1^0$		
A I	113635			114965		
K II	212992.9	99357.5	16230	215018.8	100053	16326.4
Ca III	328580.4	115587.5	(16133)	331398.6	116379	(16521)
Sc IV	(460300)	(131720)	(16080)	(464300)	(132901)	(16299)
Ti V	(608100)	(147800)	(15859)	(613500)	(149200)	(16225)
V VI	771759	(163659)	(15692)	778925	(165425)	(15990)
Cr VII	951110	179351	(15839)	960340	181415	(16045)
Mn VIII	(1146300)	(195190)		(1157800)	(197460)	

to draw a correction curve, and thus the wavelength may be in error by 0.01Å.

In Table II are listed the series limits calculated from two members of the $^1S_0 - ms\ ^1P_1^0$ series (designated by $L(^1P_1^0)$), and the limits $L(^3P_1^0)$ calculated from two members of the $^1S_0 - ms\ ^3P_1^0$ series. In the third column are listed, for purposes of comparison, the 1S_0 term values previously reported.¹ In the fourth column are the differences $L(^1P_1^0) - L(^3P_1^0)$ and in the fifth column the doublet splitting of the ground state, $^2P_{3/2\ 1/2}$ of the chlorine-like ions A II, K III, etc.

The $^1P_1^0$ and $^3P_0^0$ terms in A I approach the $^2P_{1/2}$ state of A II as a limit, and the $^3P_1^0$ and $^3P_2^0$ terms approach the $^2P_{3/2}$ state of A II. The data in Table II show that this is true for all ions of the A I - Mn VIII isoelectronic sequence. The difference between the limits $L(^1P_1^0)$ and $L(^3P_1^0)$ compares favorably with the known values of the $^2P_{3/2\ 1/2}$ splitting in K III and Ca IV, and with the predicted splitting in V VII and Cr VIII. This prediction is made by assuming the regular trend of the screening constant s with changing Z in the expression for the regular doublet law:

$$\Delta\nu = R\alpha^2(Z-s)^4/n^3l(l+1).$$

A graph of s vs. Z is shown in Fig. 3.

The only accurately known deepest term values in the A I - Mn VIII sequence are those

of A I and K II, viz., 1S_0 of A I is $127,103.8\ \text{cm}^{-1}$ and 1S_0 of K II is $256,637\ \text{cm}^{-1}$. The $L(^3P_1^0)$ limits are deeper than the correct values in both these cases but in V VI and in Cr VII the $L(^3P_1^0)$ limits are not as deep as the previously¹ reported 1S_0 term values. However, the $L(^3P_1^0)$ limits are more nearly correct for the latter cases since they are the result of a limit calculation rather than an extrapolation. The $L(^3P_1^0)$ values for V VI and Cr VII should not be in error by more than ± 0.5 percent. This can be seen from Table III, which gives the results of a calculation of the series limit $L(^3P_1^0)$ from two members of the $^1S_0 - ms\ ^3P_1^0$ series in the Ne I - Si V sequence and in A I, Kr I, Rb II and Xe I, all of which are rare gas-like, and have similar spectra. Data for the Ne I - Si V sequence are taken from Söderqvist's monograph.⁹ The other data are from Bacher and Goudsmit.

In Table IV are listed the ionization potentials of the members of the A I - Mn VIII isoelectronic sequence, and in Table V are listed the values of the deepest terms.

The Moseley diagram from which the interpolations and extrapolations in Tables II and V are made is shown in Fig. 4.

The data used to construct Figs. 1 and 2 are shown in Tables VI and VII.

⁹ J. Söderqvist, Nova Acta Reg. Soc. Sci. Upsaliensis, (VI) 9, No. 7, p. 102 (1934).