RP 89

THE FIRST SPECTRUM OF KRYPTON

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ABSTRACT

The older data on the first spectrum of krypton being inadequate for an analysis, discharge tubes were prepared with krypton gas of high purity and operated to emit the spectrum of neutral Kr atoms. About 200 lines (3302.54 to 9751.77 A) characterizing the first spectrum of krypton were photographed with concave grating and quartz spectrographs. From these spectrograms a new list of estimated intensities and measured wave lengths was obtained.

Analysis of these new data led to the identification of the main spectral terms analogous to those of the similarly constructed neon and argon spectra. Practically all of the Kr I lines have been classified in series of various types. From the combinations and series limits absolute term values are derived, and the ionization potential of 13.940 volts is deduced for Kr. The general features of the Kr I spectrum are found to be closely analogous to those of the preceding rare gases Ne I and A I, and in excellent accord with the theoretical expectations.

The proposal that the krypton line 5649.56 A be substituted for the cadmium line 6438.4696 A as a primary standard of wave length is discussed. The proposed krypton standard has relatively low intensity, and it involves a metastable level. These objections do not apply to the stronger line 5870.92 A, but it can not be recommended as a standard until it has been reexamined for hyperfine structure.

CONTENTS

I. INTRODUCTION

Ramsay and Travers [1] discovered a new constituent of atmospheric air in 1898. They called it krypton (Kr) and indicated that its spectrum was characterized by two brilliant lines for which the approximate wave lengths 5867.7 and 5568.8 A were reported. Runge [2] in 1899 pointed out that, spectroscopically, krypton bears a close analogy to argon. Like argon it emits two different line spectra, one without

[1] Ramsay and Travers, Proc. Roy. Soc., 63, p. 405; 1898.
[2] Runge, Astrophys. J. 10, p. 73; 1899.

Leyden jar and spark gap in the secondary circuit of an induction coil, the other with Leyden jar and spark gap. He published the wave lengths for 16 lines (4274.09 to 7601.47 A) in the first spectrum, and 31 lines (3654.11 to 5419.38 A) in the second. The analogy of the first spectrum of krypton to the red spectrum of argon was further borne out by the discovery that the wave numbers of several pairs of lines showed equal differences, three pairs of lines with the difference 945 being noted by Runge.

Lists of wave lengths were also given by Liveing and Dewar [3] but only approximate values were obtained. A more complete and accurate determination of wave lengths for both spectra of krypton was completed by Baly [4] in 1903. He gave 74 lines (3502.69 to 6456.65 A) for the first spectrum and 733 lines (2418.13 to 5871.12 A) for the second, but the stronger lines are common to both lists and some in each are identifiable with xenon. For a quarter of a century Baly's results have held first place as the most comprehensive and accurate description of the krypton spectra. An extension to the longer waves was made in 1919 by Merrill,[5] who published the wave lengths of 41 lines (6421.1 − 8928.72 A) characterizing the first spectrum of krypton. Approximate values for the wave lengths of 24 red lines (5994 to 7595) of the first spectrum of Kr were reported by Collie.[6] An attempt to measure more Kr I lines was made by Otsuka [7] in 1926, but he was able to observe only 55 lines (3665.32 to 8112.91 A) before his spectrum tubes became inoperative. Contributions to the spectra of krypton in the extreme ultra-violet have been made by Hertz and Abbink,[8] by Taylor,[9] and by Abbink and Dorgelo.[10]

The electrodeless discharge was employed by L. Bloch, E. Bloch, and Déjardin [11] to separate various stages of krypton spectra, but no new information was obtained for the first spectrum.

In addition to these general descriptions of the emission spectra of krypton, a number of investigations have been made with interferometers to determine the wave lengths of some of the stronger lines relative to the primary standard, the red radiation from Cd (6438.4696 A). The first of these was by Buisson and Fabry [12] who measured the wave lengths of the bright green and yellow lines as 5570.2908 and 5870.9172 A, respectively. Meggers [13] determined the wave lengths of 17 of the stronger lines (4273.9696 to 7601.544 A) and

[3] Liveing and Dewar, Proc. Roy. Soc., **68**, p. 389; 1901.
[4] Baly. Phil. Trans., **202**, p. 183; 1904.
[5] Merrill, B. S., Sci. Papers, **15**, No. 345, p. 251; 1919.
[6] Collie, Proc. Roy. Soc., **97**, p. 349; 1920.
[7] Otsuka, Zeit. f. Phys., **36**, p. 786; 1926.
[8] Hertz and Abbink, Naturw., **14**, p. 648; 1926.
[9] Taylor, Proc. Nat. Acad. Sci., **12**, p. 658; 1926.
[10] Abbink and Dorgelo, Zeit. f. Phys., **47**, p. 221; 1928.
[11] L. Bloch, E. Bloch, and Déjardin, Ann. de. Phys. (10), **2**, p. 461; 1924.
[12] Buisson and Fabry, Comptes Rendus, **156**, p. 945; 1913.
[13] Meggers, B. S. Sci. Papers, **17**, p. 193; 1921.

found 5570.2872 and 5870.9137 for the green and yellow lines. The latter lines were measured by Perard [14] who obtained 5570.2892 and 5870.9154 for their values. Finally Weber [15] measured three lines of Kr (5649.5924, 5870.9463, and 6456.3241) relative to Cd (6438.5033 A in air at 20° C., 760 mm Hg and 10 mm water vapor), and proposed the yellow-green line (5649.5924 A) as a primary standard to replace the red line of Cd.

Sixteen of the stronger krypton lines (4273 – 5870 A) were examined with Lummer-Gehrcke interferometer plates by Gehrcke and Janicki;[16] they report that all the lines are sharp, especially 5570 and 5870 A. According to Perard,[17] who studied the latter lines with a Michelson interferometer, each has two close satellites. It is our intention to examine the Kr lines with a Fabry-Perot etalon of Adam Hilger's construction and to determine the hyperfine structure of complex lines.

The International Conference of Weights and Measures [18] in 1927 provisionally adopted the red radiation from Cd (6438.4696 A) as the primary standard of wave length, but recommended that the krypton line (565 mμ) be investigated with a view of its eventual substitution for the red ray of Cd.

This action of the conference is responsible in part for the present investigation. Since certain properties of spectral lines (pressure effect, reversibility, Zeeman effect, relative intensity) are now known to be related to the spectral terms (atomic energy levels) it appeared desirable first to classify the spectrum lines so as to be able to draw upon theoretical considerations in a discussion of the suitability of a line as a standard wave length. Before the structure of the Kr I spectrum could be successfully analyzed it was necessary to make an entirely new description of the spectrum, since the older data are entirely inadequate for this purpose. The present paper, therefore, deals with a preliminary description and with the interpretation of the Kr I spectrum. In later publications, we expect to give other data on interferometer comparisons of wave lengths, studies of hyperfine structure, detection of fainter lines, and extensions of series to higher members.

As already stated, the first regularities among krypton lines were discovered by Runge in 1899. Additional constant differences between wave numbers were found by Paulson [19] in 1914 and by Merrill in 1919.

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[14] Perard, Comptes Rendus, **176**, p. 1060; 1923.
[15] Weber, Physik. Zeit., **29**, p. 233; 1928.
[16] Gehrcke and Janicki, Ann. der Phys., **81**, p. 314; 1926.
[17] Perard, Comptes Rendus, **184**, p. 447; 1927.
[18] Seventh Conf. Gen. des Poids et Mesures, p. 52; 1927.
[19] Paulson, Ann. d. Phys., **45**, p. 428; 1914.

More recently, McLennan and Ruedy [20] undertook absorption experiments with excited krypton to assist in identifying the metastable levels. Seven infra-red lines were found to show absorption, but the terms which they involve were not identified. Ten lines of shorter wave length were reported to be associated with the separation of 4,930 cm^{-1}; only one pair appears to be real.

In a recent paper announcing the discovery of new lines in various rare gas spectra Gremmer [21] mentions having observed three new lines (5672.4, 5993.7, and 9751.7 A) in the Kr I spectrum, and he presents a table of $1s_i - 2p_k$ combinations which involve mostly infrared lines.

Two additional papers dealing with the structure of krypton spectra must be mentioned for the sake of completeness, although they contribute nothing of value to the subject. They are by Hicks [22] and by Williams.[23]

II. WAVE-LENGTH MEASUREMENTS

The sources of radiation were glass or fused quartz tubes of the "dumb-bell" type described by Nutting [24] or by Meggers.[25] The bulbs contained aluminum disk electrodes 1 inch (25 mm) diameter, and the capillary connecting the bulbs in the case of the glass tubes had a bore of about 2 mm while in the quartz tube it was less than 1 mm. These tubes were used "side-on," a three or four fold magnified image of the capillary being projected on the slit of the spectrograph. The tubes were filled in this laboratory with gas purchased from the Linde Gesellschaft für Eismaschinen in Höllriegelskreuth b. München. Samples of both Kr and Xe were obtained, the arc spectra of both were measured and compared throughout the entire range accessible to photography; they reveal the only impurities as traces of H and Hg in each, a trace of Xe in Kr and a minute trace of Kr in Xe. Comparison of the two spectra observed under similar conditions has made possible for the first time a perfect separation of the lines and proper assignment of each to the element it characterizes. The identification of Xe lines in the Kr spectra was greatly facilitated by the variable intensity of the impurity lines. Owing to the gradual adsorption of the heavier rare gases coincident with electrode evaporation, the Xe lines became progressively weaker in the Kr tubes as their time of service increased so that after 50 to 100 hours discharge the Xe lines practically disappeared while the Kr lines remained as intense as ever. In a similar manner, the Hg

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[20] McLennan and Ruedy, Trans. Roy. Soc. Can. (3), **22**, p. 15; 1928.
[21] Gremmer, Zeit. f. Phys., **50**, p. 716; 1928.
[22] Hicks, Phil. Trans., A **220**, p. 335; 1919.
[23] Williams, Ciencias Físicas y Matemáticas (No. 82), p. 255; 1928.
[24] Nutting, B. S. Sci. Papers, **4**, p. 511; 1907.
[25] Meggers, B. S. Sci. Papers, **12**, p. 202; 1915.

lines decreased in intensity until they almost vanished in the older tubes.

Most investigators of Kr spectra have remarked upon the rapidity with which electrode sputtering usually takes place and the accompanying gradual disappearance of the gas. Under such conditions the tube gradually increases in resistance until the discharge shows spark lines (the second spectrum) and finally ceases altogether when the tube appears to have become vacuous. Sometimes a portion of the gas can be released by heating, but sooner or later it becomes necessary to fill the tubes with a fresh supply of gas. This adsorption of the gas occurs most readily and rapidly in tubes filled at a low pressure so that the dark space surrounding the electrodes reaches the walls of the tube; it is extremely slow when the pressure is high enough to constrict the dark space to 1 mm or less. We have filled our tubes with a gas pressure corresponding to about 10 mm Hg. Several of them have been operated from 100 to 200 hours each, and although metallic deposits from the electrodes have gradually accumulated on the walls the arc spectrum still appears to be as intense as it was originally.

To emit the arc spectrum the Kr tubes have been operated with a. c. transformers by connecting the electrodes directly to the secondary terminals without encumbering the circuit with extra inductances, condensers, or spark gaps. Two different transformers have been employed, one rated to give 10,000 volts and the other 40,000 volts, the former being used to excite the quartz tube illuminating a quartz spectrograph and the latter for the operation of glass tubes photographed with a diffraction grating spectrograph. The primaries in each case were connected to 110 volts, 60 cycles, the current being 3 to 4 amperes in the smaller transformer and 10 to 12 in the larger. With these discharges the tubes emitted almost perfectly pure arc spectra (Kr I), only a few of the most intense spark lines (Kr II) appearing very faintly.

Most of the spectrograms were made in the first (and second) order of a 6-inch Anderson grating with 7,500 lines per inch, giving a scale of 10.4 A in the first order. This grating has a radius of curvature of 21 feet and is illuminated with parallel light in a Wadsworth mounting which has been described in other papers.[26] These spectrograms were supplemented by others made with an E_1 Hilger autocollimating quartz-spectrograph especially to record faint lines in the ultra-violet where the principal series converge.

For the longer wave spectral regions, the photographic plates were sensitized with pinaflavol, pinaverdol and pinacyanol, dicyanin, rubrocyanin, and neocyanin. The exposure times ranged from 12 to

[26] Meggers and Burns, B. S. Sci. Papers, 18, p. 191; 1922.

50 hours, but little or no advantage was gained by exposing longer than 20 or 24 hours.

Comparison spectra of iron were superposed before and after each of the long exposures to Kr, and wave-length determinations were made relative to the secondary standards in the spectrum of the iron arc. Acknowledgments are due to Bourden F. Scribner for making most of the wave-length computations. The majority of the lines were measured on four or more spectrograms, and the error of the mean in such cases is probably not more than one or two hundredths of an Angstrom unit. This accuracy of the wave lengths in relative value is attested by the combination principle and series relations presented below.

So far as we are aware, except for a colored drawing of 20 lines reproduced in a paper by Ramsay and Travers,[27] no map of the krypton arc spectrum has ever been published. To remedy this deficiency, we are reproducing in Figures 1, 2, 3, and 4 portions of our spectrograms showing the first spectrum of krypton from its limit in the ultra-violet near 3300 A to the longest wave length, 9751 A, which we have been able to photograph in the infra-red. In addition to the intense green and yellow lines which dominate the visible spectrum, the most striking feature of this spectrum is the group of intense lines in the blue-violet (4274 to 4502 A) and a similar group of even stronger lines in the infra-red. The plates made with the grating and glass tubes were remarkably free from continuous background, but the exposures made with the quartz spectrograph exhibited some special features deserving mention. The quartz tube used for these exposures has an extra fine capillary. It showed an intense Kr I spectrum, a small number of impurity lines of Xe, a few of the stronger Hg lines, one or two lines of the Balmer series of H, 2 Si lines and in addition a strong continuous background extending over the entire spectrum, superposed upon which was a peculiar distribution of fine lines suggesting band structure. It may be that the continuous background arises from some sort of fluorescence in the quartz capillary; we have been unable to identify the groups of fine lines. Suspecting that they might be parts of known band spectra, selected by unique conditions of the discharge, attempts were made to identify them with the secondary spectrum of hydrogen and with cyanogen bands, but no correspondence could be found with these or with any known band spectrum. They may be due to some silicon compound or unrecognized impurity. Although a band spectrum is ascribed to He, none has ever been mentioned for any of the other rare gases.

These fine lines appear mainly in two groups, one in the ultra-violet (3064 to 3270 A) and the other in the violet (4050 to 4250 A);

[27] Ramsay and Travers, Phil. Trans., A 197, p. 47; 1901.

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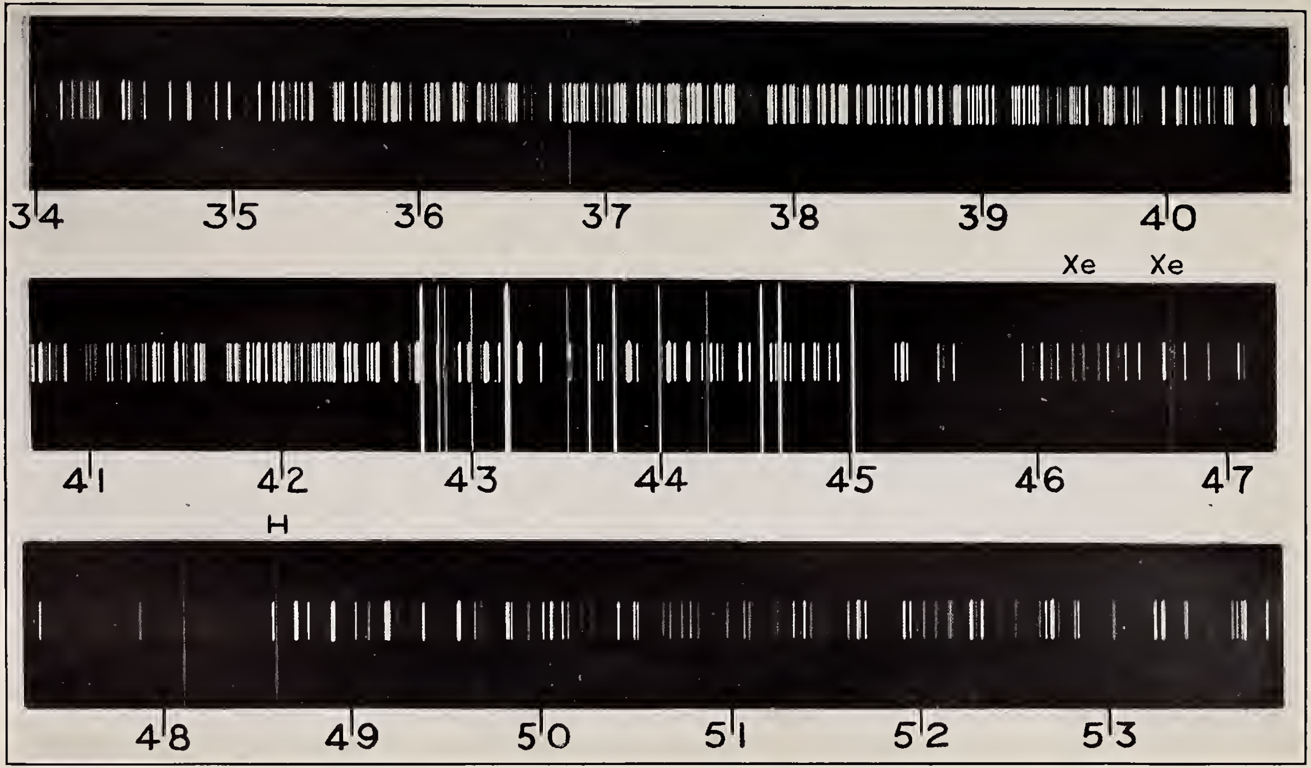

FIGURE 1.—*Arc spectrum of krypton (3400 A to 5400 A) with comparison spectrum of iron*

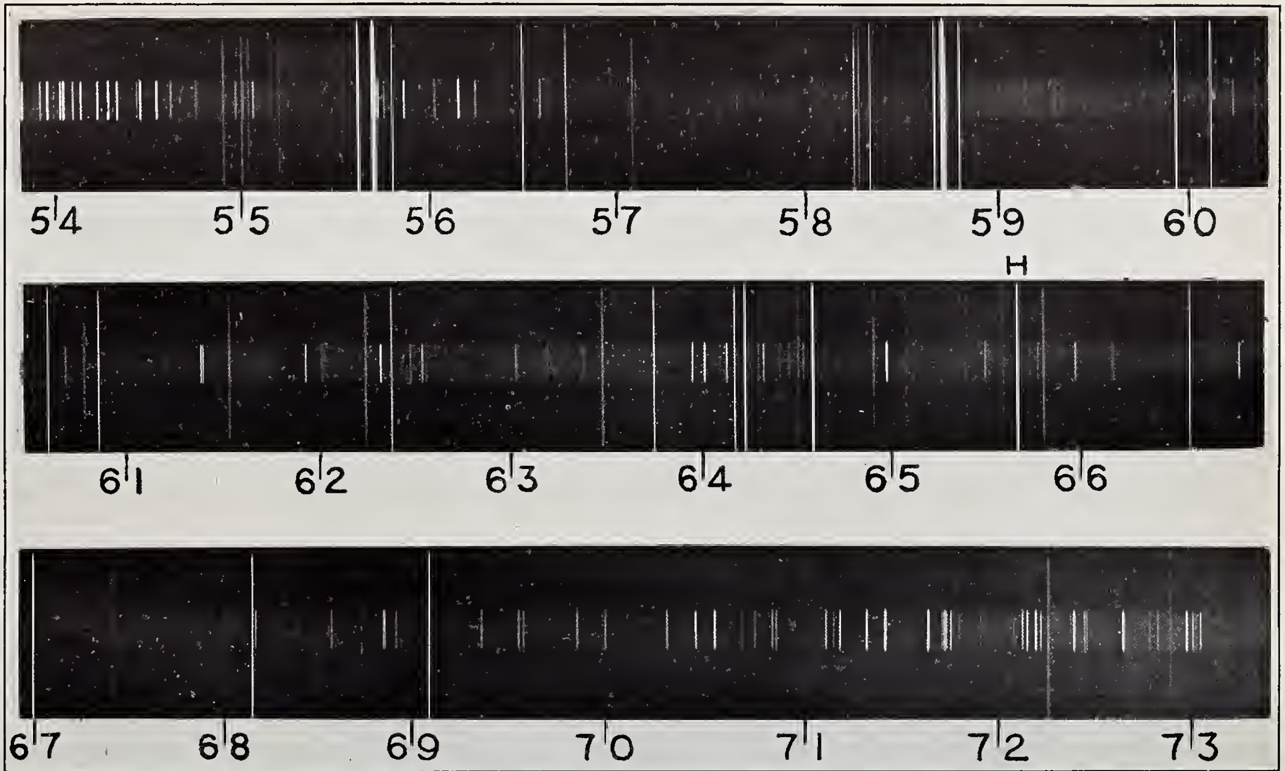

FIGURE 2.—*Arc spectrum of krypton (5400 A to 7340 A) with comparison spectrum of iron*

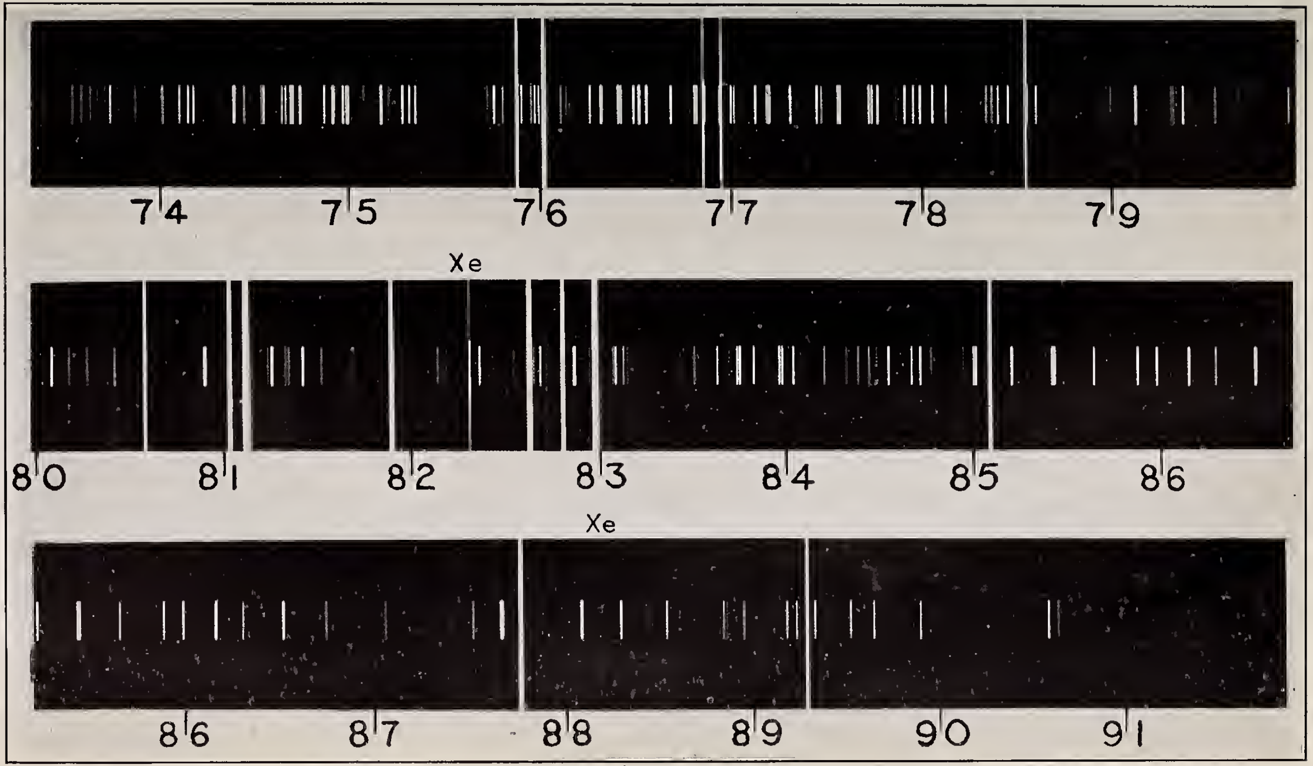

Figure 3.—*Arc spectrum of krypton (7340 A to 9200 A) with comparison spectrum of iron*

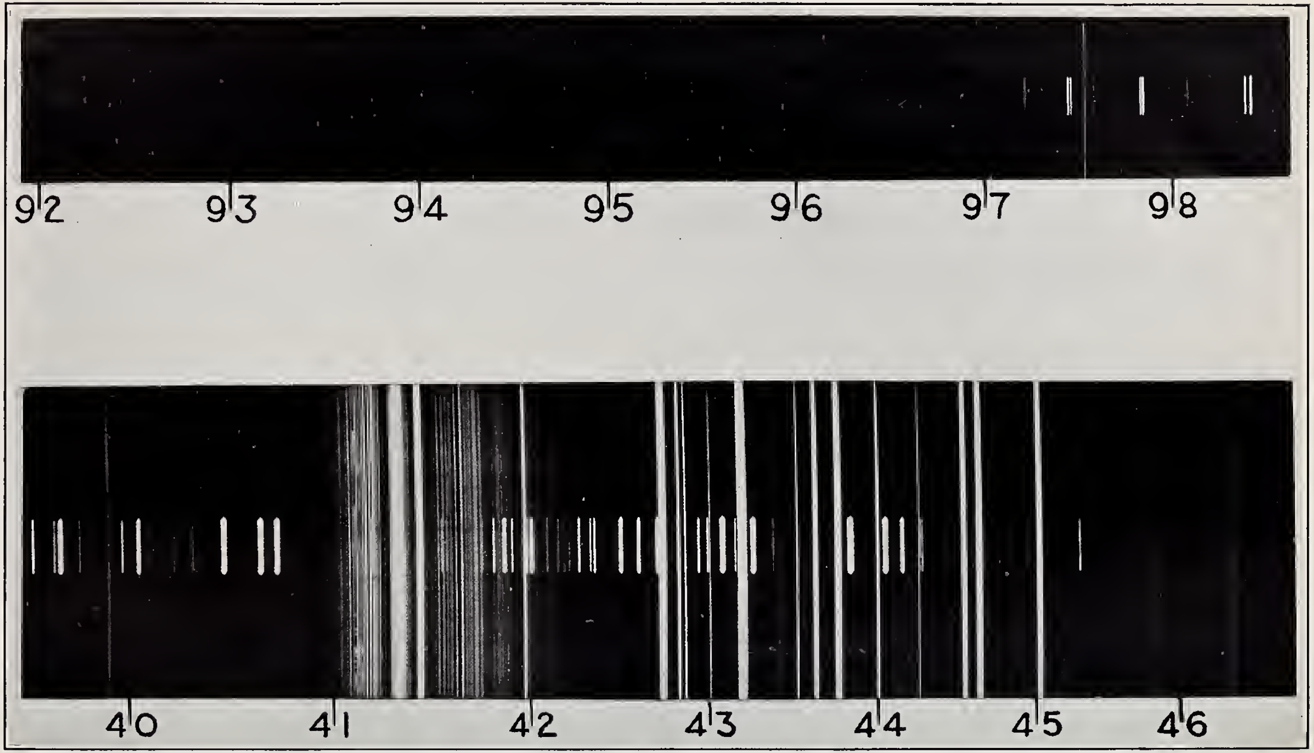

FIGURE 4.—*Arc spectrum of krypton (9200 A to 9850 A) and (3960 A to 4700 A), each with comparison spectrum of iron*

the former may be identifiable with H_2O. The latter group is the more prominent; it is reproduced in the last spectrogram in Figure 4, from an enlargement of a prismatic spectrogram which may be compared with a grating spectrogram of nearly the same scale in Figure 1, the grating spectrograms were made with glass tubes having capillary bore of 2 mm and only the strongest exposures with these tubes show the main lines of this band very faintly. We have not determined whether or not current density or applied potential accounts for this difference in the behavior of the quartz and glass tubes.

III. ANALYSIS OF THE Kr I SPECTRUM

1. THEORETICAL TERMS; COORDINATION TO SERIES LIMITS

In the unexcited state of neutral krypton (Z=36) the atomic configuration has a closed shell with two 4*s* and six 4*p* electrons symbolized by $4s^2\ 4p^6$. According to Hund's [28] theory the spectral term which characterizes the normal state is a single level, $^1S_0$. The terms which represent the excited states of the atom result from the interaction of the series electron with the electron group $s^2\ p^5$ which characterizes the unexcited state of the ion, Kr^+. The term arising from the configuration $s^2\ p^5$ is an inverted $^2P_{2,\,1}$.[29] This term has already been established for Kr II by Kichlu;[30] the levels have a separation of 5,371 cm^{-1}. We may, therefore, derive the terms representing the excited states of the neutral atom by finding the resultant obtained by adding in turn the electrons *ns*, *np*, *nd*, etc., to the term ^2P. In the following table are given the theoretical terms which may be expected to account for the first spectrum of krypton.

TABLE 1.—*Electron configurations and theoretical terms of the Kr I spectrum*

Electron configuration	Theoretical terms based on $^2P_{2,1}$ of Kr II					
$(s^2\ p^6)$		$^1S_0$				
$(s^2\ p^5)\cdot s$		$^1P_1$			$^3P_{2,1,0}$	
$(s^2\ p^5)\cdot p$	$^1S^1$	$^1P_1$	$^1D_2$	$^3S_1$	$^3P_{2,1,0}$	$^3D_{3,2,1}$
$(s^2\ p^5)\cdot d$	$_1P^1$	$^1D_2$	$^1F_3$	$^3P_{2,1,0}$	$^3D_{3,2,1}$	$^3F_{4,3,2}$

The binding of an *s*-electron thus gives 4 levels, a *p*-electron 10, and a *d*-electron a set of 12 levels. In the analogous spectra of the other rare gases, Ne I and A I, these energy levels have been established, respectively, by Paschen [31] and by Meissner.[32] In the nota-

[28] Hund, Linienspektren und periodisches system des Elemente, p. 144; Julius Springer; Berlin, 1927.
[29] For convenience in printing and reading, the inner quantum numbers of levels belonging to even multiplicities are increased by one-half.
[30] Kichlu, Proc. Roy. Soc., **A 120**, p. 643; 1928.
[31] Paschen, Ann d. Phys., **60**, p. 405; 1919; **63**, p. 201; 1920.
[32] Meissner, Zeit, f. Phys., **37**, p. 238; 1926; **39**, p. 172; 1926; **40**, p. 839; 1927.

tion introduced by Paschen, and used also by Meissner to facilitate comparison of the argon analysis with the neon data, the set of four levels was designated "s-terms," s_2, s_3, s_4, s_5 in the order of increasing magnitude. The set of 10 levels was referred to as "p-terms," $p_{1,\ 2,\ 3,\ \ldots\ 10}$, and the 12 levels as d and s' terms.

In order that the structure of the Kr I spectrum may be conveniently compared with Ne I and A I the Paschen notation will be retained in the present paper and a translation into the modern notation is added. In all three cases the designation of the 4 s-terms is the same but if the 10 p-terms are numbered in order of magnitude they must be rearranged to compare levels with the same inner quantum numbers in the different spectra. The notation for the corresponding terms in the Ne I, A I, and Kr I spectra is compared in Table 2 in Paschen's notation.

TABLE 2.—*Corresponding terms in Ne I, A I, and Kr I spectra*

j	0	1	0	2	1	2	1	2	3	1	1	0	1	2
Ne I	p_1	p_2	p_3	p_4	p_5	p_6	p_7	p_8	p_9	p_{10}	s_2	s_3	s_4	s_5
A I	p_1	p_2	p_5	p_3	p_4	p_6	p_7	p_8	p_9	p_{10}	s_2	s_3	s_4	s_5
Kr I	p_1	p_3	p_5	p_2	p_4	p_6	p_7	p_8	p_9	p_{10}	s_2	s_3	s_4	s_5

In the analyses of the Ne I and A I spectra, it was found that the terms converge to two limits, separated by a displacement constant A. These two limits are related to the ground levels $^2P_2$ and $^2P_1$ of the ion. Thus of the 10 p-terms, $p_{1,\ 2,\ 3,\ 4,}$ are coordinated to $^2P_1$, while $p_{5,\ 6\ \ldots\ 10}$ converge to $^2P_2$. The latter are called Ritzian terms because they follow the Ritz series formula, whereas the former, the non-Ritzian terms, require the addition of a constant to the term value. Similarly 8 of the d-terms go to $^2P_2$ and the other 4 to $^2P_1$ as limits. The coordination of the various terms to the series limits [33] is summarized in Table 3. We are confident that this identification of the experimental terms (in Paschen notation) with the theoretical terms is mainly correct, although it must be admitted that it is open to question in a few particulars and lacks verification of Zeeman-effect data in the case of krypton.

On the basis of Zeeman effects for neon, Goudsmit and Uhlenbeck (Zeit. f. Phys., **35**, p. 618; 1926) give the following identification of the 10 p-terms as the most probable:

$$p_1\ p_2\ p_3\ p_4\ p_5\ p_6\ p_7\ p_8\ p_9\ p_{10}\ {}^1S_0\ {}^3P_1\ {}^3P_0\ {}^3P_2\ {}^1P_1\ {}^3D_2\ {}^3D_1\ {}^1D_2\ {}^3D_3\ {}^3S_1$$

The analogous interpretation for the krypton terms is as follows:

$$p_1\ p_2\ p_3\ p_4\ p_5\ p_6\ p_7\ p_8\ p_9\ p_{10}\ {}^1S_0\ {}^3P_2\ {}^3P_1\ {}^1P_1\ {}^3P_0\ {}^3D_2\ {}^3D_1\ {}^1D_2\ {}^3D_3\ {}^3S_1$$

[33] Hund, Zeit. f. Phys., **52**, p. 601; 1928.

It does not appear possible at the present time to harmonize the deductions from Zeeman-effects and the theory of coordination to limits; in the meantime a certain amount of arbitrariness must exist in the translation of the Paschen notation into the quantum notation.

TABLE 3.—*Coordination of terms in Kr spectra*

Limits	$^2P_2$				$^2P_1$	
s-terms	$^3P_2$ s_5	$^3P_1$ s_4			$^3P_0$ s_3	$^1P_1$ s_2
p-terms	$^3D_1$ p_{10}	$^3D_3$ p_9	$^3D_2$ p_8		$^3S_1$ p_4	$^1P_1$ p_3
	$^3P_1$ p_7	$^3P_2$ p_6	$^3P_0$ p_5		$^1D_2$ p_2	$^1S_0$ p_1
	$^3P_0$ d_6	$^3P_1$ d_5	$^3F_4$ d'_4	$^3F_3$ d_4	$^3P_2$ s''_1	$^1D_2$ s''''_1
d-terms	$^3F_2$ d_3	$^3D_2$ d''_1	$^3D_3$ d'_1	$^3D_1$ d_2	$^1F_3$ s'''_1	$^1P_1$ s'_1

For the 10 *p*-terms the Russell-Saunders coupling

$$(l_1\ l_2)\ (s_1\ s_2) = (ls) = j$$

gives the following arrangement of inner quantum numbers:[34]

321, 210, 1, 2, 1, 0

The intermediate coupling

$$(\ (l_2\ s_2)\ s_1)\ l_1 = (\ (j_2 s_1)\ l_1) = j$$

or

$$(\ (\ (s_1\ s_2)\ l_2)\ l_1) = (\ (sl_2)\ l_1) = j$$

gives

321, 210, 210, 1

and the coupling

$$(\ (l_1\ s_1)\ (l_2\ s_2)\ ) = (j_1\ j_2) = j$$

gives

3210, 21, 21, 10

In neon the observed grouping of terms is

1, 3212, 1201, 0

In argon it is

1, 3212, 0121, 0

and in krypton, we find the grouping

132120, 1120

[34] Mack, Laporte, and Lang, Phys. Rev., **31**, p. 748; 1928.

The displacement constants, A, found by Paschen and by Meissner for the limits of the Ritzian and non-Ritzian series, are related to the coordination of arc spectrum levels to the two levels $^2P_{2,1}$ of the ions. This constant is, however, not exactly equal to the $^2P_{2,1}$ separation, as is shown in Table 4, where also the data for krypton have been added.

TABLE 4.—*Level separations in Ne I, A I, and Kr I*

	Neon	Argon	Krypton
$1s_5-1s_3$ } $^3P_2-^3P_0$ }	776. 90	1, 409. 92	5, 219. 90
A	780. 0	1, 423. 20	5, 330±
$^2P_{2\ 1}$	782	1, 431	5, 371
Centers of gravity of $3p$-term groups	788	1, 451	5, 353

Since the ground doublet of Kr II has a relatively large separation ($\Delta\nu=5{,}371$ cm^{-1}) it was expected that the two groups in the 10 p-terms and in the 12 d-terms would be clearly separated; this has, indeed, been found to be the case.

2. ABSOLUTE TERM VALUES; IONIZATION POTENTIAL OF Kr

In both neon and argon it was found that the mathematical representation of certain series showed irregularities which appeared as discontinuities in the graphs plotted with effective quantum numbers as ordinates and order numbers as abscissas. In both cases, however, the series $2p_9-md'_4$ gave a smooth curve indicating that it fits a Ritz formula very closely. The krypton series behave very similarly to their neon and argon analogues, but it is a striking fact that with the krypton sources used for our observations the series are relatively short and the intensity decrement is very large so that for the most part each series is traced only through 2, 3, 4, or 5 members.

For the determination of the absolute term values, it is best to extrapolate a long series following a Ritz formula without discontinuities. The series $2p_9-md'_4$ mentioned above is the most regular as well as the longest; in neon, 11 members were observed, in argon 14, and in krypton 8, omitting the first line which lies in the unobserved infra-red at 1.9 μ. We have followed the example of Meissner in basing all term values upon the limit derived from this series. The $2p_9-md'_4$ series fixes the $2p_9$ level at 20,620.87. Adding the wave number of the line $1s_5-2p_9=12{,}322.60$ places the $1s_5$ level at 32,943.47. It must be remarked that this line has been interpreted as $2p_9-3d'_4$ and $1s_5-2p_9$; it may be an unresolved doublet.

The $1s_5$ level can, however, also be calculated from other series; for example, $1s_5-mp_9$ and $1s_5-mp_6$. Furthermore, it can be calculated from the series $1s_4-mp_6$ and $1s_4-mp_7$ because the $1s_5-1s_4$ difference ($\Delta\nu=945.00$ cm^{-1}) is known. The results of these various methods of obtaining $1s_5$ are as follows:

1. Series $2p_9-md'_4$ and $\nu=1s_5-2p_9$ — $1s_5=32{,}943.47$
2. Series $1s_5-mp_9$ — $1s_5=32{,}941.54$
3. Series $1s_5-mp_6$ — $1s_5=32{,}943.65$
4. Series $1s_4=mp_7$ and $\Delta\nu=1s_5-1s_4$ — $1s_5=32{,}944.87$
5. Series $1s_4-mp_6$ and $\Delta\nu=1s_5-1s_4$ — $1s_5=32{,}943.94$

The mean of the five values is 32,943.49, practically identical with the first one, which is chosen as the basic value to which all remaining term values are referred. Any error in the level $1s_5=32{,}943.47$ is therefore the same for all the other terms.

The data for the five series mentioned above are presented in Table 5.

From the established terms, $1s_4=31{,}998.47$, $1s_2=27{,}068.57$, and the known resonance lines of krypton

$$p_0-1s_4=1{,}235.85\text{A};\ \nu=80{,}916$$
$$p_0-1s_2=1{,}164.88\text{A};\ \nu=85{,}846$$

the term value representing the normal state $^1S_0$ of the neutral krypton atom is calculated to be

$$^1S_0=112{,}914.50$$

corresponding to an ionization potential of 13.940 volts. This value is in good agreement with the estimation of Abbink and Dorgelo[35] on the absorption of spark lines (ca. 13.9 volts) but somewhat higher than the value obtained by Hertz and Kloppers[36] from critical potential measurements (ca. 13.3 volts).

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[35] Abbink and Dorgelo, Zeit. f. Phys., 47, p. 232; 1928.
[36] Hertz and Kloppers: Zeit. f. Phys., 31, p. 463; 1925.

TABLE 5.—*Determination of absolute term values*

Series $2p_9-m\,d'_4$ $(5p^3D_3-5d^3F_4)$

$$\nu=A-\frac{R}{[m+\mu+a(A-\nu)]^2}$$

$R=109{,}736.36.$
$A=20{,}620.868.$
$\mu=+0.5980788914.$
$a=+0.000004693149215.$

$m.$	Int.	$\lambda_{obs.}$	$\nu_{obs.}$	$\nu_{calc.}$	$\Delta\nu_{calc-obs.}$
2				5, 231. 214	
3	300	8, 112. 94	12, 322. 60	12, 325. 017	+2. 42
4	50	6, 456. 29	15, 484. 50	15, 484. 500	00
5	10	5, 832. 84	17, 139. 57	17, 139. 570	00
6	4	5, 520. 45	18, 109. 45	18, 109. 180	−. 27
7	3	5, 339. 07	18, 724. 65	18, 724. 483	−. 17
8	1	5, 223. 53	19, 138. 83	19, 138. 877	+. 05
9	−1	5, 144. 97	19, 431. 06	19, 431. 060	. 00
10	−1	5, 089. 02	19, 644. 69	19, 644. 708	+. 02

$\nu=12{,}322.60=1s_5-{}^2p_9.$
$1s_5=20{,}620.87+12{,}322.60=32{,}943.47.$

Series $1s_5-mp_9$. $(5s^3P_2-5p^3D_3.)$

$A=32{,}941.544.$
$\mu=+0.379381302\pm10^{-10}.$
$a=-0.00000333814841.$

$m.$	Int.	$\lambda_{obs.}$	$\nu_{obs.}$	$\nu_{calc.}$	$\Delta\nu_{calc.-obs.}$
2	300	8, 112. 94	12, 322. 60	12, 390. 266	+67. 67
3	150	4, 319. 58	23, 143. 86	23, 143. 860	. 00
4	10	3, 679. 60	27, 169. 16	27, 169. 160	. 00
5	2	3, 431. 68	29, 131. 92	29, 131. 395	−. 53
6	1	3, 306. 21	30, 237. 44	30, 237. 440	. 00

$1s_5=32{,}941.54.$

Series $1s_5-mp_6$.

$A=32{,}943.646.$
$\mu=+0.4149578862\pm10^{-10}.$
$a=-0.000002684173300.$

$m.$	Int.	$\lambda_{obs.}$	$\nu_{obs.}$	$\nu_{calc.}$	$\Delta\nu_{calc.-obs.}$
2	100	7, 601. 55	13, 151. 60	13, 276. 972	+125. 37
3	100	4, 273. 96	23, 390. 94	23, 390. 940	. 00
4	8	3, 665. 35	27, 274. 78	27, 274. 780	. 00
5	2	3, 424. 90	29, 189. 59	29, 187. 182	−2. 41
6	1	3, 302. 54	30, 271. 04	30, 271. 040	. 00

$1s_5=32{,}943.65.$

TABLE 5.—*Determination of absolute term values*—Continued

Series $1s_4-mp_7$

$A=31{,}999.868.$
$\mu=0.4024498806.$
$a=-0.000002295749196.$

m	Int.	$\lambda_{obs.}$	$\nu_{obs.}$	$\nu_{calc.}$	$\Delta\nu_{calc-obs.}$
2	300	8, 298. 12	12, 047. 53	12, 248. 58	+200. 95
3	80	4, 463. 69	22, 396. 72	22, 396. 72	. 00
4	5	3, 800. 00	26, 304. 19	26, 304. 19	. 00
5	1	3, 540. 96	28, 232. 89	28, 227. 95	−4. 94
6	1—	3, 409. 94	29, 317. 65	29, 317. 65	. 00

$1s_4=31{,}999.87.$
$1s_5-1s_4=945.00.$
$1s_5=32{,}944.87.$

Series $1s_4-mp_6$.

$A=31{,}998.942.$
$\mu=0.4145597886.$
$a=-0.000002649589035.$

m	Int.	$\lambda_{obs.}$	$\nu_{obs.}$	$\nu_{calc.}$	$\Delta\nu_{calc-obs.}$
2	150	8, 190. 10	12, 206. 51	12, 337. 28	+130. 77
3	50	4, 453. 92	22, 445. 85	22, 445. 85	. 00
4	4	3, 796. 94	26, 329. 55	26, 329. 55	. 00
5	1	3, 539. 52	28, 244. 37	28, 242. 10	−2. 27
6	1—	3, 408. 96	29, 326. 08	29, 326. 08	. 00

$1s_4=31{,}998.94.$
$1s_5-1s_4=945.00.$
$1s_5=32{,}943.94.$

3. THE PRINCIPAL SERIES, $1s_i-mp_k$

The data for 10 series of the type $1s_i-mp_k$ are presented in Table 6 where the observational data are represented by estimated intensity of the spectral line (in parentheses) followed by the wave length λ. The corresponding wave number in vacuum, ν, was computed with the aid of Kayser's "Tabelle der Schwingungszahlen," except for lines in the unobserved infra-red region which are represented by term differences. Values of m_p have been calculated from each combination, and finally the mean value of each term and the effective quantum number $\sqrt{\frac{R}{m_p}}$, associated with it, are given.

TABLE 6.—*Kr I principal series* $1s_i - mp_k$

Principal series mp_1

Limit: $1s_2$=27,068.57

Comb.	m	2	3
s_2p_1	λ ν mp_1	(20)7, 685. 25 13, 008. 37 14, 060. 10	(10)4, 351. 36 22, 974. 88 4, 093. 69
s_4p_1	λ ν mp_1	(17, 938. 27)	(27, 904. 78)
		14, 060. 20	4, 093. 69
	$\sqrt{\frac{R}{mp_1+A}}$	2. 3789	3. 4124

A=5,330.

Principal series, mp_2

Limits: $1s_2$=27,068.57
$1s_4$=31,998.47
$1s_5$=32,943.47

Comb.	m	2	3
s_2p_2	λ ν mp_2	(200)8, 263. 29 12, 098. 39 14, 970. 18	(20)4, 399. 97 22, 721. 07 4, 347. 50
s_4p_2	λ ν mp_2	(300)5, 870. 92 17, 028. 40 14, 970. 07	(4)3, 615. 47 27, 651. 06 4, 347. 41
s_5p_2	λ ν mp_2	(50)5, 562. 22 17, 973. 46 14, 970. 01	(1)3, 495. 95 28, 596. 37 4, 347. 08
Mean	mp_2	14, 970. 09	4, 347. 34
	$\sqrt{\frac{R}{mp_2+A}}$	2. 3250	3. 3674

A=5,330.

TABLE 6.—*Kr I principal series*—Continued

Principal series, mp_3
Limits: $1s_2=27,068.57$
$1s_3=27,723.57$
$1s_4=31,998.47$
$1s_5=32,943.47$

Comb.	m	2	3
s_2p_3	λ	(100)8, 281. 11	(6)4, 410. 34
	ν	12, 072. 36	22, 667. 64
	mp_3	14, 996. 21	4, 400. 93
s_3p_3	λ	(40)7, 854. 82	(10)4, 286. 45
	ν	12, 727. 53	23, 322. 79
	mp_3	14, 996. 04	4, 400. 78
s_4p_3	λ	(25)5, 879. 88	
	ν	17, 002. 45	
	mp_3	14, 996. 02	
s_5p_3	λ	(200)5, 570. 30	(3)3, 502. 53
	ν	17, 947. 38	28, 542. 65
	mp_3	14, 996. 09	4, 400. 84
Mean	mp_3	14, 996. 09	4, 400. 84
	$\sqrt{\frac{R}{mp_3+A}}$	2. 3235	3. 3581

$A=5,330.$

Principal series: mp_4
Limits: $1s_2=27,068.57$
$1s_3=27,723.57$
$1s_4=31,998.47$
$1s_5=32,943.47$

Comb.	m	2	3
s_2p_4	λ	(100)8, 508. 92	(10)4, 425. 18
	ν	11, 749. 15	22, 591. 63
	mp_4	15, 319. 42	4, 476. 94
s_3p_4	λ	(50)8, 059. 51	(8)4, 300. 47
	ν	12, 404. 30	23, 246. 75
	mp_4	15, 319. 27	4, 476. 82
s_4p_4	λ	(25)5, 993. 83	(1)3, 632. 46
	ν	16, 679. 21	27, 521. 66
	mp_4	15, 319. 26	4, 476. 81
s_5p_4	λ	(6)5, 672. 40	(1)3, 511. 86
	ν	17, 624. 34	28, 466. 83
	mp_4	15, 319. 13	4, 476. 64
Mean	mp_4	15, 319. 27	4, 476. 80
	$\sqrt{\frac{R}{mp_4+A}}$	2. 3053	3. 3451

$A=5,330.$

TABLE 6.—*Kr I principal series*—Continued

Principal series: mp_5

Limits: $1s_2$=27,068.57

$1s_4$=31,998.47

Comb.	m	2	3	4	5	6
s_2p_5	λ		(10)5,580.33	(2)4,736.06	(3)4,263.65	(1)4,086.91
	ν	8,246.23	17,915.12	21,564.02	23,449.65	24,461.48
	mp_5		9,153.45	5,504.55	3,618.92	2,607.09
s_4p_5	λ	(50)7,587.40	(70)4,376.13	(6)3,773.47	(2)3,522.65	(1)3,401.40
	ν	13,176.13	22,844.84	26,493.31	28,379.63	29,391.26
	mp_5	18,822.34	9,153.63	5,505.16	3,618.84	2,607.21
Mean	mp_5	18,822.34	9,153.54	5,504.86	3,618.88	2,607.15
	$\sqrt{\frac{R}{mp_5}}$	2.4145	3.4624	4.4646	5.5067	6.4876

Principal series: mp_6

Limits: $1s_2$=27,068.57

$1s_4$=31,998.47

$1s_5$=32,943.47

Comb.	m	2	3	4	5	6
s_2p_6	λ		(4)5,707.47			
	ν	7,276.65	17,516.05			
	mp_6		9,552.52			
s_4p_6	λ	(150)8,190.10	(50)4,453.92	(4)3,796.94	(1)3,539.52	(1−)3,408.96
	ν	12,206.51	22,445.85	26,329.55	28,244.37	29,326.08
	mp_6	19,791.96	9,552.62	5,668.92	3,754.10	2,672.39
s_5p_6	λ	(100)7,601.55	(100)4,273.96	(8)3,665.35	(2)3,424.90	(1)3,302.54
	ν	13,151.60	23,390.94	27,274.78	29,189.59	30,271.04
	mp_6	19,791.87	9,552.51	5,668.69	3,753.88	2,672.43
Mean	mp_6	19,791.92	9,552.56	5,668.85	3,753.99	2,672.41
	$\sqrt{\frac{R}{mp_6}}$	2.3546	3.3893	4.3997	5.4067	6.4080

TABLE 6.—*Kr I principal series*—Continued

Principal series: mp_7

Limits: 1 s_2=27,068.57
1 s_3=27,723.57
1 s_4=31,998.47
1 s_5=32,943.47

Comb.	m	2	3	4	5	6
s_2p_7	λ ν mp_7	7,117.77	(2) 5,723.50 17,466.99 9,601.58			
s_3p_7	λ ν mp_7	7,772.77	(3) 5,516.56 18,122.22 9,601.35		(1) 4,172.75 23,958.27 3,765.83	(1) 3,992.01 25,042.98 2,680.59
s_4p_7	λ ν mp_7	(300)8,298.12 12,047.63 19,950.84	(80) 4,463.69 22,396.72 9,601.75	(5)3,800.60 26,304.19 5,694.28	(1)3,540.96 28,232.89 3,765,58	(1) 3,409.94 29,317.65 2,680.82
s_5p_7	λ ν mp_7	(30) 7,694.52 12,992.71 19,950.76	(20) 4,282.94 23,341.90 9,601.57	(2) 3,668.76 27,249.43 5,694.03		
Mean	mp_7	19,950.80	9,601.56	5,694.16	3,765.58	2,680.70
	$\sqrt{\frac{R}{mp_7}}$	2.3453	3.3807	4.3899	5.3984	6.3980

Principal series: mp_8

Limits: 1 s_2=27,068.57
1 s_4=31,998.47
1 s_5=32,943.47

Comb.	m	2	3	4
s_2p_8	λ ν mp_8	6,460.69	(1) 5,787.13 17,274.94 9,793.63	
s_4p_8	λ ν mp_8	(150) 8,776.80 11,390.55 20,607.92	(60) 4,502.35 22,204.42 9,794.05	(3) 3,812.24 26,223.88 5,774.59
s_5p_8	λ ν mp_8	(100) 8,104.37 12,335.63 20,607.84	(50) 4,318.57 23,149.32 9,794.15	(10) 3,679.60 27,169.16 5,774.31
Mean	mp_8	20,607.88	9,793.94	5,774.45
	$\sqrt{\frac{R}{mp_8}}$	2.3075	3.3474	4.3593

TABLE 6.—*Kr I principal series*—Continued

Principal series: mp_9

Limit: $1s_5$=32,943.47

Comb.	m	2	3	4	5	6
s_5p_9	λ	(300)8, 112. 94	(150)4, 319. 58	(10)3, 679. 60	(2)3, 431. 68	(1)3, 306. 24
	ν	12, 322. 60	23, 143. 86	27, 169. 16	29, 131. 92	30, 237. 17
	mp_9	20, 620. 87	9, 799. 61	5, 774. 31	3, 811. 55	2, 706. 30
	$\sqrt{\frac{R}{mp_9}}$	2. 3069	3. 3463	4. 3593	5. 3657	6. 3678

Principal series: mp_{10}

Limits: $1s_2$=27,068.57
$1s_3$=27,723.57
$1s_4$=31,998.47
$1s_5$=32,943.47

Comb.	m	2	3	4	5
s_2p_{10}	λ		(20)5, 866. 75	(2)4, 724. 84	(2)4, 302. 41
	ν	5, 321. 85	17, 040. 50	21, 158. 84	23, 236. 27
	mp_{10}		10, 028. 07	5, 909. 73	3, 832. 30
s_3p_{10}	λ		(15)5, 649. 54	(3)4, 582. 80	(3)4, 184. 46
	ν	5, 976. 85	17, 695. 66	21, 814. 63	23, 891. 24
	mp_{10}		10, 027. 91	5, 908. 94	3, 832. 33
s_4p_{10}	λ	(3)9, 751. 77	(5)4, 550. 30		
	ν	10, 251. 75	21, 970. 43		
	mp_{10}	21, 746. 72	10, 028. 04		
s_5p_{10}	λ	(100)8, 928. 73	(50)4, 362. 64	(1)3, 698. 01	(1)3, 434. 10
	ν	11, 196. 75	22, 915. 48	27, 033. 90	29, 111. 40
	mp_{10}	21, 746. 72	10, 027. 99	5, 909. 57	3, 832. 07
Mean	mp_{10}	21, 746. 72	10, 028. 00	5, 909. 65	3, 832. 23
	$\sqrt{\frac{R}{mp_{10}}}$	2. 2463	3. 3079	4. 3092	5. 3512

Table 6 verifies the statement made before that the ten $1s_i$-mp_k series are separated into two groups, $p_{1, 2, 3, 4}$ going to the higher level ($^2P_1$) of the ion, and $p_{5, 6} \ldots {}_{10}$ to the lower level ($^2P_2$). Since the $1s-mp_{1, 2, 3, 4}$ series are short, having only two members each, it is not possible to determine the displacement constant A accurately. Assuming that the change in quantum defects for the $2p_{1, 2, 3, 4}$ and $3p_{1, 2, 3, 4}$ terms is of the same order as for the terms $mp_{5, 6} \ldots {}_{10}$ following the Ritz formula the displacement constant turns out to be about 5,330.

Another approximation can be obtained with the aid of Landé's center-of-gravity rule. It has been shown by Landé [37] that for neon

[37] Back-Landé, Zeemaneffekt u. Multipletstruktur, Julius Springer, Berlin, 1925, p. 58.

the separation of the center of gravity of the 2-term groups ($p_{1,\,2,\,5,\,4}$) and ($p_{3,\,7,\,10,\,6,\,8,\,9}$) has nearly the same value as the displacement constant A, and with higher order number approaches this magnitude. The analogous groups in krypton are ($p_{1,\,3,\,4,\,2}$) and ($p_{5,\,7,\,10,\,6,\,8,\,9}$). The separation of the centers of gravity of these two groups amounts to 5,420 for the $2p$ terms, and 5,353 for the $3p$ terms.

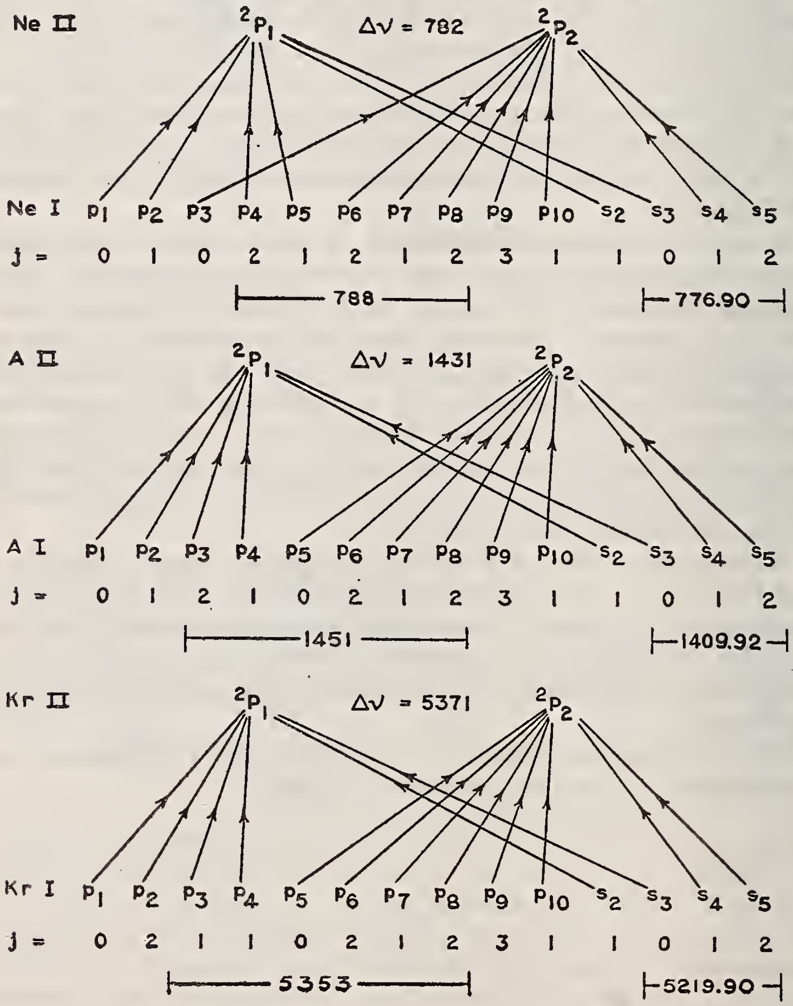
Both approximations, 5,330 from the series limits and 5,353 from the center-of-gravity calculation, are in close agreement with the separation of the $^2P_{2,\,1}$ levels of Kr^+ which is 5,371 cm^{-1}. From the term table, it is seen that the center of gravity of the $3p_{1,\,2,\,3,\,4}$ term group will have the value of about 420 so that these terms are already very high and would be expected to give only very faint lines. Thus it is apparent that the large separation of the $^2P_{2,\,1}$ levels of the Kr ion is partly responsible for the relative simplicity of the observed Kr I spectrum.

It may be questioned whether the p_1 term is correctly identified since the combinations with the $1s_4$ level are not present. After ordering the lines in the *sp* and *pd* series only the strong line at 7685.25 A remained. Assuming that this is the lacking $1s_2-2p_1$ combination puts the $2p_1$ term in the region where it must be expected, and the effective quantum number also supports this interpretation. The absence of other expected combinations can not be explained, but similar cases occur in other spectra; for example, $1s_2-2p_5$, $1s_5-4p_{10}$, $1s_5-5p_{10}$, and $1s_5-4p_4$, which are expected to be relatively strong are entirely absent in argon.

No lines of the principal series can be expected shorter than 3034 A, and between this limit and the resonance line at 1236 A no krypton arc lines can be present. Above this limit some additional faint lines may be observable; further investigation of these with a brighter source will be important for the extension of some of the relatively short series.

The corresponding terms in Ne I, A I, and Kr I spectra and their coordination to limits are compared in Table 7.

TABLE 7.—*Corresponding terms in Ne I, A I, and Kr I spectra, and their coordination to limits in Ne II, A II, and Kr II spectra*



4. THE X AND Y SERIES

Paschen found in the Ne I spectrum some terms which he could not identify, so he labeled them x and y terms. In the A I spectrum Meissner found similar terms which he called X, Y, and Z terms. Important characteristics of these unidentified terms are that they begin with order No. 4 and are hydrogenlike; thus in neon, these terms have effective quantum numbers 3.9937 and 3.9939, in argon 3.9813, 3.9932, and 3.9937. In krypton four such terms have been found; their effective quantum numbers are 3.9726, 4.9746, 3.9896, and 4.9693.

Judging from the effective quantum numbers, Meissner suspected that these terms came from an f-electron. The addition of an f-electron to the ($s^2\ p^5$) configuration of krypton would give rise to the term group

$$^1D_2,\ ^1F_3,\ ^1G_4,\ ^3D_{1,\ 2,\ 3},\ ^3F_{2,\ 3,\ 4},\ ^3G_{3,\ 4,\ 5}.$$

Only one level, $^3D_1$ can combine with the four s-levels, and it is possible that this is the correct interpretation of our mX terms. For the mY terms there remains a choice between $^3D_2$, $^3F_2$, $^1D_2$, but it seems most likely that they should be identified as $^3D_2$ since the separation between the mX and mY terms is relatively small.

Data for the X and Y series of krypton are collected in Table 8 which is arranged in the same way as Table 6.

TABLE 8.—*The X and Y series*

Series mX

Limits: $1s_2$=27,068.57
$1s_3$=27,723.57
$1s_4$=31,998.47
$1s_5$=32,943.47

Comb.	m	4	5	6
s_2X	λ	(5d) 4, 969. 17	(3) 4, 416. 84	(1−) 4, 167. 26
	ν	20, 118. 49	22, 634. 28	23, 989. 84
	mX	6, 950. 08	4, 434. 29	3, 078. 73
s_3X	λ	(6) 4, 812. 61	(1) 4, 292. 64	(1−) 4, 056. 39
	ν	20, 772. 96	23, 289. 16	24, 645. 53
	mX	6, 950. 61	4, 434. 41	3, 078. 04
s_4X	λ	(5) 3, 991.13		(1−) 3, 456. 80
	ν	25, 048. 50		28, 920. 23
	mX	6, 949. 97		3, 078. 21
s_5X	λ	(3) 3,846. 06	(1) 3, 506. 67	
	ν	25, 993. 29	28, 508. 96	
	mX	6, 950. 18	4, 434. 51	
Mean	mX	6, 950. 21	4, 434. 40	3, 078. 40
	$\sqrt{\frac{R}{mpX}}$	3. 9726	4. 9746	5. 9705

TABLE 8.—*The X and Y series*

Series mY

Limits: $1\ s_2=27{,}068.57$
$1\ s_4=31{,}998.47$
$1\ s_5=32{,}943.47$

Comb.	m	4	5
s_2Y	λ	(3) 4, 955. 22	(5) 4, 418. 74
	ν	20, 175. 12	22, 624. 35
	mY	6, 893. 45	4, 444. 22
s_4Y	λ	(1) 3, 982. 26	(2) 3, 628. 12
	ν	25, 104. 29	27, 554. 66
	mY	6, 894. 18	4, 443. 81
s_5Y	λ	(5) 3, 837. 87	(1) 3, 507. 87
	ν	26, 048. 75	28, 499. 21
	mY	6, 894. 72	4, 444. 26
Mean	mY	6, 893. 68	4, 444. 10
	$\sqrt{\frac{R}{mY}}$	3. 9896	4. 9693

5. THE SUBORDINATE SERIES

All the observed combinations of md_i and ms_i levels with the mp_i terms are collected in Table 9. It is seen from this table that numerous combinations which can be expected on the basis of the assigned inner quantum numbers have not been observed, some on account of faintness and others because they lie in the unexplored infra-red. Further efforts to record fainter lines will be necessary to test some of the tentatively assigned inner quantum numbers.

The combinations with the non-Ritzian term group, $2p_{1,\ 2,\ 3,\ 4}$ are expected in the far infra-red. Strong combinations, both ps and pd, are expected in the spectral region between 1 μ and 2 μ; the wave lengths can be calculated from the terms with considerable precision.

Table 9 also shows that the group of four d-terms coordinated to $^2P_1$ is not yet found. First, it was supposed that some of the terms now interpreted as higher d-terms represented this group, but since these terms were later found to be in series with the lower d-terms the earlier point of view was discarded. It is further seen from Table 9 that the non-Ritzian terms are already high even with relatively low order number. This is no doubt the reason that the observed spectrum is mainly due to combinations with terms coordinated to the lower $^2P_2$ level of the Kr ion. One may expect that this feature will be still further developed in the arc spectrum of xenon.

TABLE 9.—*The subordinate series*

18,822.34 19,791.92 19,950.80 20,607.88 20,620.87 21,746.72 112,914.50

969.58 158.88 657.08 12.99 1,125.85

j	Term value	Term symbol	$^2p_5$	$^2p_6$	$^2p_7$	$^2p_8$	$^2p_9$	$^2p_{10}$	p_0
			18,822.34	19,791.92	19,950.80	20,607.88	20,620.87	21,746.72	112,914.50
3	9, 213. 84	$4d'_1$				(1)11, 393. 99	(2)11, 407. 08		
1	9, 113. 43	$4d_5$				(1)11, 494. 47		(5)12, 633. 27	(2)103, 803
0	8, 393. 70	$4d_6$						(5)13, 353. 02	
4	8, 298. 27	$4d'_4$					(100)12,322.60		
3	7, 998. 83	$4d_4$				(4)12, 609. 08	(1)12, 622. 00		
2	7, 907. 97	$4d_3$		(2)11, 883. 95				(5)13, 838. 74	
2	7, 751. 72	$4d''_1$			(2)12, 199. 06	(1)12, 856. 17			
1	7, 267. 46	$3s$		(2)12, 524. 22		(1)13, 340. 88	(5)13, 353. 02+	(10)14, 479. 03	(4)105, 645
1	7, 144. 49	$4d_2$	(1)11, 677. 93		(1)12, 806. 24	(3)13, 463. 35		(3)14, 602. 24	(3)105, 772
	6, 452. 01	x		(1)13, 340. 17				(3)15, 294. 44	
0	5, 311. 57	$5d_6$			(1)14, 639. 4			(10)16, 435. 15	
1	5, 238. 90	$5d_5$		(4)14, 552. 94	(1)14, 712. 15	(3)15, 368. 95		(20)16, 507. 69	
4	5, 136. 37	$5d'_4$					(50)15, 484. 50		
2	5, 118. 27	$5d_3$		(8)14, 673. 65	(4)14, 832. 62		(4)15, 502. 58	(20)16, 628. 47+	
3	5, 038. 30	$5d_4$				(30)15, 569. 53	(8)15, 582. 61		
2	4, 922. 37	$5d''_1$		(1)14, 869. 8	(10)15, 028. 45	(8)15, 685. 49	(1)15, 698. 52		
3	4, 868. 83	$5d'_1$		(15)14, 923. 09		(3)15, 739. 08	(5)15, 752. 02		
2	4, 590. 11	$4s$		(5)15, 201. 77	(1)15, 360. 76	(3)16, 017. 80	(10)16, 030. 72	(6)17, 156. 57	
1	4, 541. 94	$5d_2$	(1)14, 280. 3	(3)15, 249. 90	(5)15, 408. 82	(6)16, 065. 88		(2)17, 204. 98	
0	3, 584. 02	$6d_6$			(1)16, 366. 49			(4d)18, 162. 98	

TABLE 9.—*The subordinate series*—Continued

j	Term value	Term symbol	$^2p_5$	$^2p_6$	$^2p_7$	$^2p_8$	$^2p_9$	$^2p_{10}$	p_0
1	3, 572. 26	$6d_5$	(3)15, 249. 90+	(3)16, 219. 70				(6)18, 174. 60	
2	3, 539. 84	$6d_3$		(5)16, 252. 13	(1)16, 411. 06		(1)17, 080. 97	(5)18, 206. 87	
4	3, 481. 30	$6d'_4$					(10)17, 139. 57		
3	3, 443. 72	$6d_4$			(20)16, 507. 69+	(8)17, 164. 14	(4)17, 177. 17		
2	3, 387. 57	$6d''_1$			(4)16, 563. 26	(3)17, 220. 28			
3	3, 336. 02	$6d'_1$		(5)16, 455. 82		(1)17, 271. 89	(2)17, 284. 83		
2	3, 163. 03	$5s$		(20)16, 628. 47+		(1)17, 444. 90	(3)17, 457. 72	(2)18, 583. 76	
1	3, 135. 82	$6d_2$			(2)16, 814. 96	(2)17, 472. 18			
1	2, 811. 72			(1)16, 980. 2	(10)17, 139. 57+			(1)18, 935. 00	
1	2, 579. 47	$7d_5$		(1)17, 212. 34				(2)19, 167. 38	
4	2, 511. 42	$7d'_4$					(4)18, 109. 45		
3	2, 406. 97	$7d'_1$		(2)17, 384. 68			(1)18, 214. 2		
2	2, 402. 13	$7d_3$		(1)17, 389. 58				(1)19, 344. 85	
2	2, 306. 71	$6s$					(1h)18, 313. 73	(7)19, 440. 01	
3	1, 867. 90					(2)18, 740. 17		(1)19, 878. 63	

6. THE Kr I SPECTRUM IN THE EXTREME ULTRA-VIOLET

The following krypton arc lines in the extreme ultra-violet have been reported (Table 10) by Abbink and Dorgelo.[38]

TABLE 10.—*First spectrum of Kr in the extreme ultra-violet*

Line No.	Int.	λ	(Obs.)	(Calc.)	Combination
1	30	1, 235. 85	80, 916. 0		$p_o - 1s_4$
2	20	1, 164. 88	85, 846. 0		$p_o - 1s_2$
3	(3)	1, 134. 89	88, 114. 3		
4	(3)	1, 134. 15	88, 171. 8		
5	5	1, 003. 54	99, 647. 3		$p_o - 3d_5$
6	7	1, 001. 09	99, 891. 1		$p_o - 2s_4$
7	2	963. 36	103, 803	103, 801. 07	$p_o - 4d_5$
8	(3)	953. 42	104, 886	104, 886. 60	$p_o - 2s_2$
9	4	946. 57	105, 645	105, 647. 04	$p_o - 3s_2$
10	3	945. 43	105, 772	105, 770. 01	$p_o - 4d_2$

The adherence of lines 3, 4, and 8 to the first spectrum of krypton is admitted to be doubtful. The first pair (1,235.85 and 1,164.88 A) are the resonance lines which we have used in connection with our terms to calculate the ionization potential of krypton. (See p. 139.) Lines 5, 6, 7, 9, and 10, respectively, fix the following levels: 13,267, 13,023, 9,111, 7,269, and 7,142.

Comparison with our term table (Table 9, p. 151) shows that the last three are identifiable with our levels 9,113.96, 7,267.46, and 7,144.49. In argon, a group of five strong lines on the short wavelength side of the resonance lines is explained by combinations of p_0 with $3d_5$, $2s_4$, $3d_2$, $2s_2$, and $3s_1'$ which are the levels with the inner quantum number $j=1$. Five lines have also been observed in krypton, but it is doubtful if these lines involve the same levels as in argon.

On account of the large displacement constant A for krypton, we interpret the 13,267 level as $3d_5$, the lowest of the group, in analogy with argon. The 13,023 level is probably $2s_4$; its effective quantum number is 2.9024, in agreement with the effective quantum number of $1s_4$, viz, 1,8519.

The doubtful doublet at 1134 A would give levels in a region where no terms can be expected; these lines can not belong to the first spectrum of krypton. The remaining line at 953 A was also doubtful, but it appears to be real; it involves a level at 8,028 identifiable with our level 8,027.90 separated 4,995 cm $^{-1}$ from the $2s_4$ level at 13,023, the former being identified as $2s_2$ since the separation $s_4 - s_2$ which is 4,930 cm $^{-1}$ in the $1s$ group must approach the $^2P_{2,1}$ separation (5,371 cm $^{-1}$), of the ion.

[38] Abbink and Dorgelo, Zeit. f. Phys. 47, p. 221; 1928.

An interpretation is thus given of all the lines ascribed to the first spectrum of krypton in the extreme ultra-violet. From analogy with argon more krypton lines may be expected in this region, and further attempts to record fainter lines will be important for the identification of certain levels which still remain doubtful.

7. IDENTIFICATION OF THE EXPERIMENTAL TERMS

In Table 11 we give a complete list of the Kr I terms. The first column contains the added electron.

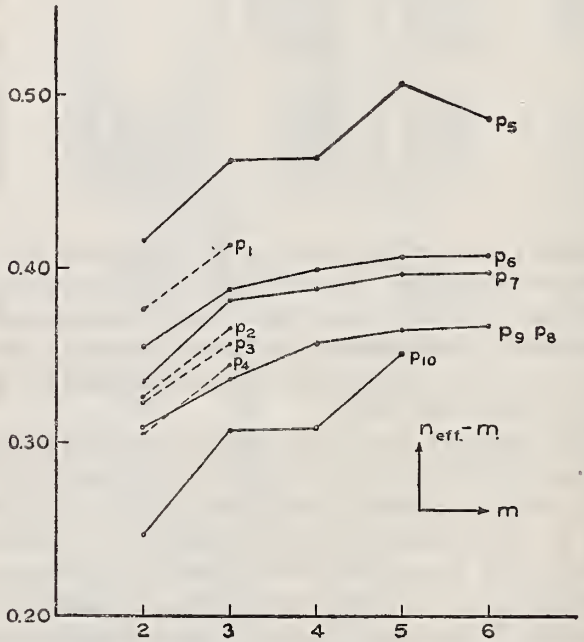


FIGURE 5.—*Effective quantum numbers for p-terms*

The inner quantum numbers are given in column 2. The Paschen notation is presented in the third column, and the remaining columns contain alternately the term values and the corresponding effective quantum numbers. The latter are an excellent criterion for the arrangement of terms in series, and when they are plotted as a function of the order number they present some interesting facts and relations. Such plots are shown in Figures 5 and 6, *p* terms in the former, *d* and *s* terms in the latter. Comparison with similar diagrams published for argon reveal further analogies between the Kr I spectrum and the A I spectrum.

Thus, Figure 5 compared with argon shows that in both cases the series converging to the upper limit $^2P_1$ are shorter than those coordi-

Table 11.—*Terms and effective quantum numbers of Kr I*

Electron	j	Term Paschen notation		m = 1		2		3		4		5	
p	0	p_0	112, 914. 50 =13. 940 volts										
s	2	s_5		32, 943. 47	1. 8251	(13, 500±)							
	1	s_4		31, 998. 47	1. 8519	13, 023	2. 9024	7, 267. 46	3. 8857				
	0	s_3		27, 723. 57	1. 8220	(8, 300±)							
	1	s_2		27, 068. 57	1. 8404	8, 027. 90	2. 8662						
p	1	p_{10}				21, 746. 72	2. 2463	10, 028. 00	3. 3079	5, 909. 65	4. 3092	3, 832. 18	5. 3512
	3	p_9				20, 620. 87	2. 3069	9, 799. 61	3. 3463	5, 774. 31	4. 3593	3, 811. 55	5. 3657
	2	p_8				20, 607. 88	2. 3075	9, 793. 94	3. 3474	5, 774. 45	4. 3593	3, 809. 29	5. 3672
	1	p_7				19, 950. 80	2. 3453	9, 601. 56	3. 3807	5, 694. 16	4. 3899	3, 765. 58	5. 3984
	2	p_6				19, 791. 92	2. 3546	9, 552. 56	3. 3893	5, 668. 85	4. 3997	3, 753. 99	5. 4067
	0	p_5				18, 822. 34	2. 4145	9, 153. 54	3. 4624	5, 504. 86	4. 4618	3, 618. 88	5. 5067
	1	p_4				15, 319. 27	2. 3053	4, 476. 80	3. 3451				
	1	p_3				14, 996. 09	2. 3235	4, 400. 84	3. 3581				
	2	p_2				14, 970. 09	2. 3250	4, 347. 34	3. 3674				
	0	p_1				14, 060. 20	2. 3789	4, 098. 69	3. 4124				
f	1	X								6, 950. 21	3. 9726	4, 434. 40	4. 9746
	2	Y								6, 893. 68	3. 9896	4, 441. 10	4. 9693
d	0	d_6								8, 393. 70	3. 6157	5, 311. 57	4. 5453
	1	d_5						13, 267	2. 8760	9, 113. 43	3. 4700	5, 238. 90	4. 5766
	4	d'_4								8, 298. 27	3. 6364	5, 136. 37	4. 6222
	2	d_3								7, 907. 97	3. 7254	5, 118. 27	4. 6304
	3	d_4								7, 998. 83	3. 7039	5, 038. 30	4. 6670
	2	d''_1								7, 751. 72	3. 7625	4, 922. 37	4. 7215
	3	d'_1								9, 213. 84	3. 4511	4, 868. 83	4. 7480
	1	d_2								7, 144. 49	3. 9191	4, 541. 94	4. 9154
	2(1)	s								7. 267. 46	3 8857	4, 590. 11	4. 8895

Electron	j	Term Paschen notation	m = 6		7		8		9		10		11	
p	0	p_0												
s	2	s_5												
	1	s_4												
	0	s_3												
	1	s_2												
p	1	p_{10}												
	3	p_9	2, 706. 30	6. 3678										
	2	p_8												
	1	p_7	2, 680. 82	6. 3980										
	2	p_6	2, 672. 43	6. 4080										
	0	p_5	2, 607. 43	6. 4876										
	1	p_4												
	1	p_3												
	2	p_2												
	0	p_1												
f	1	X	3, 078. 40	5. 9705										
	2	Y												
d	0	d_6	3, 584. 02	5. 5335	2, 624. 77	6. 4659	1, 981. 07	7. 4370						
	1	d_5	3, 572. 26	5. 5426	2, 579. 47	6. 5226	1, 911. 99	7. 5759						
	4	d'_4	3, 481. 30	5. 6144	2, 511. 42	6. 6102	1, 896. 22	7. 6073	1, 482. 04	8. 6049	1, 189. 81	9. 6033	976. 18	10. 6025
	2	d_3	3, 539. 84	5. 5679	2, 402. 10	6. 7590								
	3	d_4	3, 443. 72	5. 6450	2, 444. 62	6. 6977	1, 867. 71	7. 6651	1, 464. 47	8. 6564				
	2	d''_1	3, 387. 57	5. 6912	2, 418. 41	6. 7361								
	3	d'_1	3, 336. 02	5. 7353	2, 406. 97	6. 7518								
	1	d_2	3, 135. 82	5. 9157										
	2(1)	s	3, 163. 03	5. 8901	2, 306. 71	6. 8907								

nated to $^2P_2$. The plots of $n_{eff}-m$ for p_6 and p_7 series run parallel. This is also true for the p_8 and p_9 series; in krypton they are practically identical and so could not be separated in the diagram. The term sequences p_5 and p_{10} are most irregular, but the discontinuities are of the same type for both series in krypton as well as in argon.

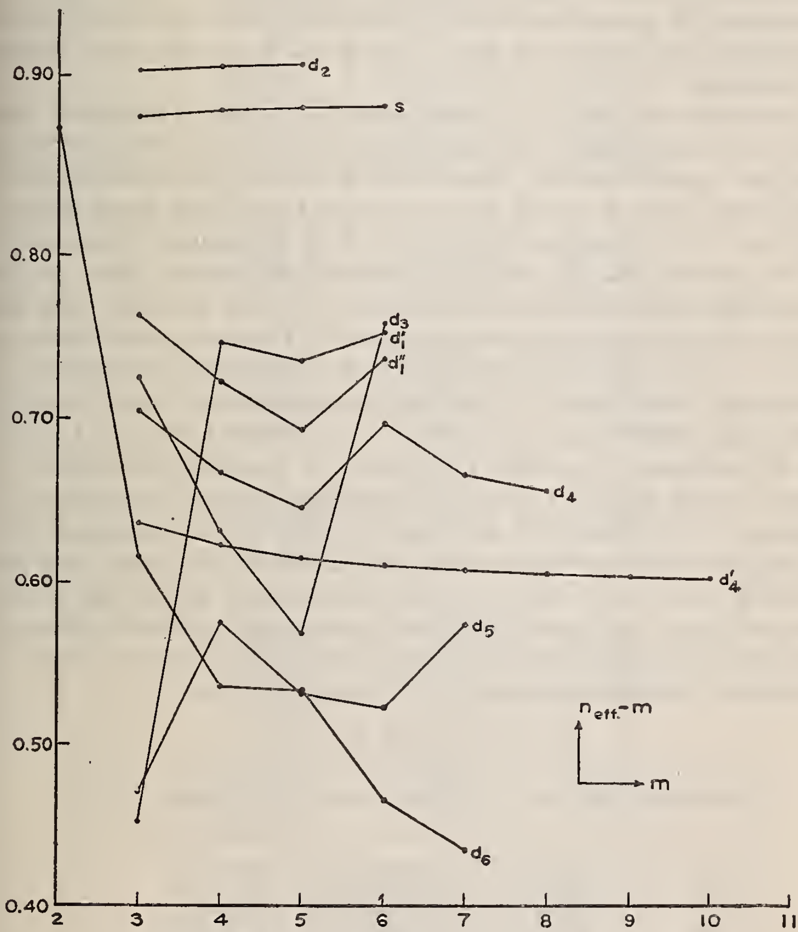


FIGURE 6.—*Effective quantum numbers for d- and s- terms*

Comparison of Figure 6 with the corresponding diagram for argon attracts attention to the following analogies. In both cases the d'_4 series gives the most perfect smooth curve; the curves for d''_1 and d_4 are irregular, but of the same type; the d_2 series is well separated from the others; most of the remaining series are very irregular and dissimilar.

8. LIST OF Kr I LINES

A complete list of the observed lines characteristic of the first spectrum of krypton is presented in Table 12, in which the estimated intensities appear in the first column, the wave lengths (international scale) in the second, wave numbers (vacuum) in the third, and level combinations in the fourth. Almost all of the 205 observed lines are accounted for as combinations of established terms presented in the preceding table, only a few lines, most of which are very faint, remain unclassified.

Four infra-red lines, 8272, 8199, and 7746, 7682 A constitute two pairs with separations 107.7 or 820.0 cm^{-1}, but the terms involved have not been identified. Some other faint lines; for example, 6410, 5977, 5887, 5279 A appear to be connected with new terms 3226.84 and 2811.7, the nature of which can not be determined at present.

The general features of this classification parallel those of the preceding rare gases, neon and argon, and are also in accord with the structure expected on theoretical grounds. The metastable character of the s_3 and s_5 levels is confirmed by the absorption observations of McLennan and Ruedy.[39] Further investigation of fainter lines in certain spectral regions, and study of the infra-red between 1 μ and 2 μ by radiometric methods, is desirable to establish the identity of certain terms which can now be suggested only with reservation. Zeeman effects, which are at present lacking for krypton lines, will be of great value in determining the nature of the terms and the coupling which is present. It will be extremely interesting to see how the g-sum rule, which has been checked only for the $2p$ terms of neon, holds for the other rare gases, especially for higher terms in connection with the coordination to the series limits.

TABLE 12.—*List of Kr I lines*

Intensity	Wave length	Wave number	Comb.
3	9, 751. 77	10, 251. 75	$1s_4-2p_{10}$
1−	8, 978. 11	11, 135. 15	
100	8, 928. 73	11, 196. 75	$1s_5-2p_{10}$
150	8, 776. 80	11, 390. 55	$1s_4-2p_8$
1	8, 774. 15	11, 393. 99	$2p_8-4d'_1$
2	8, 764. 08	11, 407. 08	$2p_9-4d'_1$
1−	8, 697. 45	11, 494. 47	$2p_8-4d_5$
1	8, 560. 81	11, 677. 93	$2p_5-4d_2$
1	8, 548. 44	11, 694. 83	
100	8, 508. 92	11, 749. 15	$1s_2-2p_4$
1−	8, 498. 15	11, 764. 02	$2p_6-2s_2$
2	8, 412. 40	11, 883. 95	$2p_6-4d_3$
1−	8, 386 62	11, 920. 48	
1−	8, 351. 22	11, 971. 01	
300	8, 298. 12	12, 047. 53	$1s_4-2p_7$

[39] McLennan and Ruedy, Trans. Roy. Soc. Can., 22 (3), p. 15; 1928.

TABLE 12.—*List of Kr I lines*—Continued

Intensity	Wave length	Wave number	Comb.
100	8, 281. 11	12, 072. 36	$1s_2-2p_3$
3	8, 272. 41	12, 085. 06	+819. 90
200	8, 263. 29	12, 098. 39	$1s_2-2p_2$
1−	8, 209. 67	12, 177. 42	
1	8, 199. 41	12, 192. 66	+820. 11
2	8, 195. 10	12, 199. 06	$2p_7-4d''_1$
150	8, 190. 10	12, 206. 51	$1s_4-2p_6$
300	8, 112. 94	12, 322. 60	$1s_5-2p_9$ $2p_9-4d_4$
100	8, 104. 37	12, 335. 63	$1s_5-2p_8$
50	8, 059. 51	12, 404. 30	$1s_3-2p_4$
1	8, 026. 36	12, 455. 53	
2	7, 982. 34	12, 524. 22	$2p_6-3s$
1−	7, 946. 99	12, 579. 93	$2p_8-2s_2$
4	7, 928. 61	12, 609. 08	$2p_8-4d_4$
1	7, 920. 50	12, 622. 00	$2p_9-4d_4$
5	7, 913. 43	12, 633. 27	$2p_{10}-4d_5$
40	7, 854. 82	12, 727. 53	$1s_3-2p_3$
1	7, 806. 55	12, 806. 24	$2p_7-4d_2$
1	7, 776. 23	12, 856. 17	$2p_8-4d''_1$
4	7, 746. 83	12, 904. 96	−819. 90
30	7, 694. 52	12, 992. 71	$1s_5-2p_7$
20	7, 685. 25	13, 008. 37	$1s_2-2p_1$
1	7, 682. 65	13, 012. 77	−820. 11
100	7, 601. 55	13, 151. 60	$1s_5-2p_6$
50	7, 587. 40	13, 176. 13	$1s_4-2p_5$
1	7, 520. 51	13, 293. 32	
1	7, 494. 01	13, 340. 17	$2p_8-x_3$
1	7, 493. 70	13, 340. 88	$2p_8-3s_2$
5	7, 486. 87	13, 353. 02	$2p_{10}-4d_6$ $2p_9-3s$
3	7, 425. 53	13, 463. 35	$2p_8-4d_2$
4	7, 287. 25	13, 718. 82	$2p_{10}-2s_2$
5	7, 224. 10	13, 838. 74	$2p_{10}-4d_3$
1	7, 000. 73	14, 280. 3	$2p_5-5d_2$
10	6, 904. 64	14, 479. 03	$2p_{10}-3s$
4	6, 869. 57	14, 552. 94	$2p_6-5d_5$
3	6, 846. 38	14, 602. 24	$2p_{10}-4d_2$
1	6, 829. 0	14, 639. 4	$2p_7-5d_6$
8	6, 813. 06	14, 673. 65	$2p_6-5d_3$
1	6, 795. 23	14, 712. 15	$2p_7-5d_5$
4	6, 740. 04	14, 832. 62	$2p_7-5d_3$
1	6, 723. 2	14, 869. 8	$2p_6-5d''_1$
15	6, 699. 18	14, 923. 09	$2p_6-5d'_1$
10	6, 652. 21	15, 028. 45	$2p_7-5d''_1$
5	6, 576. 37	15, 201. 77	$2p_7-4s$
3	6, 555. 61	15, 249. 90	$2p_6-5d_2$ $2p_5-5d_5$
3	6, 536. 52	15, 294. 44	$2p_{10}-x$
1	6, 508. 30	15, 360. 76	$2p_7-4s$
3	6, 504. 83	15, 368. 95	$2p_8-5d_5$
5	6, 488. 00	15, 408. 82	$2p_7-5d_2$
50	6, 456. 29	15, 484. 50	$2p_9-5d'_4$

TABLE 12.—*List of Kr I lines*—Continued

Intensity	Wave length	Wave number	Comb.
4	6, 448. 76	15, 502. 58	$2p_9-5d_3$
30	6, 421. 03	15, 569. 53	$2p_8-5d_4$
8	6, 415. 64	15, 582. 61	$2p_9-5d_4$
2	6, 410. 12	15, 596. 03	$2p_5-3226.33$
8	6, 373. 56	15, 685. 49	$2p_8-5d''_1$
1	6, 368. 27	15, 698. 52	$2p_9-5d''_1$
3	6, 351. 86	15, 739. 08	$2p_8-5d'_1$
5	6, 346. 64	15, 752. 02	$2p_9-5d'_1$
3	6, 241. 33	16, 017. 80	$2p_8-4s$
10	6, 236. 30	16, 030. 72	$2p_9-4s$
6	6, 222. 65	16, 065. 88	$2p_8-5d_2$
3	6, 163. 64	16, 219. 70	$2p_6-6d_5$
5	6, 151. 34	16, 252. 13	$2p_6-6d_3$
1	6, 108. 36	16, 366. 49	$2p_7-6d_6$
1	6, 091. 77	16, 411. 06	$2p_7-6d_3$
10	6, 082. 84	16, 435. 15	$2p_{10}-5d_6$
5	6, 075. 20	16, 455. 82	$2p_6-6d'_1$
20	6, 056. 11	16, 507. 69	$2p_{10}-5d_5$
4	6, 035. 79	16, 563. 26	$2p_8-6d''_1$
20	6, 012. 12	16, 628. 47	{ $2p_{10}-5d_3$ $2p_6-5s$
25	5, 993. 83	16, 679. 21	$1s_4-2p_4$
1	5, 977. 6	16, 724. 5	$2p_7-3,226.3$
2	5, 945. 42	16, 814. 96	$2p_7-6d_2$
1	5, 933. 53	16, 848. 72	
1	5, 887. 6	16, 980. 2	$2p_6-2,811.72$
25	5, 879. 88	17, 002. 45	$1s_4-2p_3$
300	5, 870. 92	17, 028. 40	$1s_4-2p_2$
20	5, 866. 75	17, 040. 50	$1s_2-3p_{10}$
1	5, 852. 85	17, 080. 97	$2p_9-6d_3$
10	5, 832. 84	17, 139. 57	$2p_9-6d'_4$
6	5, 827. 06	17, 156. 57	$2p_{10}-4s$
8	5, 824. 49	17, 164. 14	$2p_9-6d_4$
4	5, 820. 07	17, 177. 17	$2p_9-6d_4$
2	5, 810. 73	17, 204. 78	$2p_{10}-5d_2$
1	5, 808. 18	17, 212. 34	$2p_6-7d_5$
3	5, 805. 50	17, 220. 28	$2p_8-6d''_1$
1	5, 788. 15	17, 271. 89	$2p_8-6d'_1$
1	5, 787. 13	17, 274. 94	$1s_2-3p_8$
2	5, 783. 82	17, 284. 83	$2p_9-6d'_1$
2	5, 750. 60	17, 384. 68	$2p_6-7d'_1$
1	5, 748. 98	17, 389. 58	$2p_6-7d_3$
1	5, 730. 75	17, 444. 90	$2p_8-5s$
3	5, 726. 54	17, 457. 72	$2p_9-5s$
2	5, 723. 50	17, 466. 99	$1s_2-3p_7$
2	5, 721. 80	17, 472. 18	$2p_8-6d_2$
4	5, 707. 47	17, 516. 05	$1s_2-3p_6$
1	5, 702. 15	17, 532. 39	$2p_7-7d''_1$
6	5, 672. 40	17, 624. 34	$1s_5-2p_4$
15	5, 649. 54	17, 695. 66	$1s_3-3p_{10}$
1	5, 629. 64	17, 758. 21	

TABLE 12.—*List of Kr I lines*—Continued

Intensity	Wave length	Wave number	Comb.
10	5, 580. 33	17, 915. 21	$1s_2-3p_5$
2	5, 575. 56	17, 930. 45	$1s_3-3p_8$
200	5, 570. 30	17, 947. 38	$1s_5-2p_3$
50	5, 562. 22	17, 973. 46	$1s_5-2p_2$
4	5, 520. 45	18, 109. 45	$2p_9-7d'_4$
3	5, 516. 56	18, 122. 22	$1s_3-3p_7$
4*d*	5, 504. 18	18, 162. 98	$2p_8-7d_4$ $2p_{10}-6d_6$
6	5, 500. 66	18, 174. 60	$2p_{10}-6d_5$
5	5, 490. 91	18, 206. 87	$2p_{10}-6d_3$
1	5, 488. 7	18, 214. 2	$2p_9-7d'_1$
1*h*	5, 458. 87	18, 313. 73	$2p_9-6s$
2	5, 379. 55	18, 583. 76	$2p_{10}-5s$
3	5, 339. 07	18, 724. 65	$2p_9-8d'_4$
2	5, 334. 65	18, 740. 17	$2p_8-8d_4$
1	5, 279. 76	18, 935. 00	$2p_{10}-2,811.72$
3	5, 228. 14	19, 121. 95	$2p_{10}-7d_6$
1	5, 223. 53	19, 138. 83	$2p_9-9d'_4$
1	5, 222. 28	19, 143. 41	$2p_8-9d_4$
2	5, 215. 75	19, 167. 38	$2p_{10}-7d_5$
1	5, 167. 90	19, 344. 85	$2p_{10}-7d_3$
1−	5, 144. 97	19, 431. 06	$2p_9-10d'_4$
1−	5, 142. 60	19, 440. 01	$2p_{10}-6s$
1	5, 057. 90	19, 765. 65	$2p_{10}-8d_6$
1	5, 040. 26	19, 834. 73	$2p_{10}-8d_5$
1	5, 029. 13	19, 878. 63	$2p_{10}-8d_4$
5*d*	4, 967. 17	20, 118. 49	$1s_2-4X$
3	4, 955. 22	20, 175. 12	$1s_2-4Y$
6	4, 812. 61	20, 772. 96	$1s_3-4X$
2	4, 724. 84	21, 158. 84	$1s_2-4p_{10}$
2	4, 636. 06	21, 564. 02	$1s_2-4p_5$
5	4, 550. 30	21, 970. 43	$1s_4-3p_{10}$
60	4, 502. 35	22, 204. 42	$1s_4-3p_8$
80	4, 463. 69	22, 396. 72	$1s_4-3p_7$
50	4, 453. 92	22, 445. 85	$1s_4-3p_6$
10	4, 425. 18	22, 591. 63	$1s_2-3p_4$
5	4, 418. 74	22, 624. 55	$1s_2-5Y$
3	4, 416. 84	22, 634. 28	$1s_2-5X$
6	4, 410. 34	22, 667. 64	$1s_2-3p_3$
20	4, 399. 97	22, 721. 07	$1s_2-3p_2$
1	4, 383. 85	22, 804. 61	
70	4, 376. 13	22, 844. 84	$1s_4-3p_5$
50	4, 362. 64	22, 915. 48	$1s_5-3p_{10}$
10	4, 351. 36	22, 974. 88	$1s_2-3p_1$
150	4, 319. 58	23, 143. 86	$1s_5-3p_9$
50	4, 318. 57	23, 149. 32	$1s_5-3p_8$
2	4, 302. 41	23, 236. 27	$1s_2-5p_{10}$
8	4, 300. 47	23, 246. 75	$1s_3-3p_4$
1	4, 292. 64	23, 189. 16	$1s_3-5X$
10	4, 286. 45	23, 322. 79	$1s_3-3p_3$
20	4, 282. 94	23, 341. 90	$1s_5-3p_7$

TABLE 12.—*List of Kr I lines*—Continued

Intensity	Wave length	Wave number	Comb.
100	4, 273. 96	23, 390. 94	$1s_5-3p_6$
3	4, 263. 26	23, 449. 65	$1s_2-5p_5$
3	4, 184. 46	23, 891. 24	$1s_3-5p_{10}$
1	4, 172. 75	23, 950. 27	$1s_3-5p_7$
1−	3, 992. 01	25, 042. 98	$1s_3-6p_7$
5	3, 991. 13	25, 048. 50	$1s_4-4X$
1	3, 982. 26	25, 104. 29	$1s_4-4Y$
3	3, 846. 06	25, 993. 29	$1s_5-4X$
5	3, 837. 87	26, 048. 75	$1s_5-4Y$
3	3, 812. 24	26, 223. 88	$1s_4-4p_8$
5	3, 800. 60	26, 304. 19	$1s_4-4p_7$
4	3, 796. 94	26, 329. 55	$1s_4-4p_6$
6	3, 773. 47	26, 493. 31	$1s_4-4p_5$
1	3, 698. 01	27, 033. 90	$1s_5-4p_{10}$
10	3, 679. 60	27, 169. 16	$1s_5-4p_9$
2	3, 668. 76	27, 249. 43	$1s_5-4p_7$
8	3, 665. 35	27, 274. 78	$1s_5-4p_6$
1	3, 632. 46	27, 521. 66	$1s_4-3p_4$
2	3, 628. 12	27, 554. 66	$1s_4-5Y$
4	3, 615. 47	27, 651. 06	$1s_4-3p_2$
1	3, 546. 45	28, 189. 18	$1s_4-5p_8$
1	3, 540. 96	28, 232. 89	$1s_4-5p_7$
1	3, 539. 52	28, 244. 37	$1s_4-5p_6$
2	3, 522. 65	28, 379. 63	$1s_4-5p_5$
1	3, 511. 86	28, 466. 83	$1s_5-3p_4$
1	3, 507. 87	28, 499. 21	$1s_5-5Y$
1	3, 506. 67	28, 508. 96	$1s_5-5X$
1	3, 503. 87	28, 531. 74	
3	3, 502. 53	28, 542. 65	$1s_5-3p_3$
1	3, 495. 95	28, 596. 37	$1s_5-3p_2$
1	3, 456. 80	28, 920. 23	$1s_4-6X$
1	3, 434. 10	29, 111. 40	$1s_5-5p_{10}$
2	3, 431. 68	29, 131. 92	$1s_5-5p_9$
2	3, 424. 90	29, 189. 59	$1s_5-5p_6$
1	3, 409. 94	29, 317. 65	$1s_4-6p_7$
1	3, 408. 96	29, 326. 08	$1s_4-6p_6$
1	3, 401. 40	29, 391. 26	$1s_4-6p_5$
1	3, 345. 67	29, 880. 82	
1	3, 306. 24	30, 237. 17	$1s_5-6p_5$
1	3, 302. 54	30, 271. 04	$1s_5-6p_6$

IV. THE FIRST SPECTRUM OF KRYPTON AS A SOURCE OF STANDARD WAVE LENGTHS

It has been suggested that some line from the krypton spectrum might be more suitable as a primary standard of wave length than the red line (6438.4696 A) of cadmium which has been provisionally adopted as the fundamental standard, and a proposal has been made to substitute a yellow-green krypton line (5649.56 A) for the latter.

The cadmium line was selected by Michelson by empirical methods many years before any theoretical considerations based upon an analysis of the spectrum were possible. It was found experimentally that the Cd red line was very narrow, capable of a high order of interference, free from satellites or hyperfine structure, not easily reversed or absorbed. Later investigations have shown it to be only moderately sensitive to pressure and quite free from Stark effect (splitting in electric fields). Most of these properties of the Cd line can be accounted for by the methods of spectral structure analysis developed in recent years.

A theoretical consideration which favors the krypton lines is that a Kr source can be operated at a lower temperature than Cd; the Doppler motions of the radiating particles will, therefore, be smaller, the line narrower, and capable of a higher order of interference. The Doppler widening is a function of $\sqrt{\frac{T}{m}}$ where T is the absolute temperature and m is the atomic weight. On this basis xenon is the most favorable radiator.

In investigating the possibility of krypton and xenon spectra as sources of length standards of superior quality, we have begun with preliminary descriptions of the entire range of spectra which is accessible to photographic observation. As in the present case, these descriptions permit identification of the atomic energy states and classification of practically all of the spectral lines. The relative values of the energy levels and the quantum numbers associated with them give information about the individual lines and enable one to discuss their relative merits as wave-length standards. Thus the relative intensities can be derived theoretically, the susceptibility of the line to reversal or to pressure can be estimated, and the lines best qualifying as standards may then be selected for practical tests.

Analysis of the first spectrum of krypton shows that theoretical objections can be raised against the Kr green line (5649.56 A) proposed as a primary standard. First of all, the line is not sufficiently intense for general practical use. It originates with the term combination $1s_3-3p_{10}$ ($^3P_0-{}^3D_1$), thus arising from a transition between levels with small inner quantum numbers 0 and 1.

Furthermore, the final state $1s_3$ is a metastable level and lines involving such metastable levels are the first to show absorption or reversal. The yellow line of krypton (5870.92 A; 300) is estimated to be at least twenty times as intense photographically as the proposed yellow-green line (5649.56 A; 15); it arises from the term combination $1s_4-2p_2$ ($^3P_1-{}^1D_2$), thus involving stable levels with larger inner quantum numbers 1 and 2. It may be added that the relative intensities of the analogous lines in neon (6096 and 7438 A) have been measured by Dorgelo;[40] the ratio is found to be 20.5 to 1. The strong-

[40] Dorgelo, Physica, 5, p. 90; 1925.

est line of the Kr I spectrum is undoubtedly 8112.94 A, which has been classified as $2p_9-4d'_4$ ($^3D_3-{}^3F_4$) and $1s_5-2p_9$ ($^3P_2-{}^3D_3$). It is unsuited as a practical standard because it is invisible and because it is probably a blend of two lines, one of which involves the metastable level $1s_5$. The relative intensities of the neon lines analogous to $1s_3-3p_{10}$ and $1s_5-2p_9$ of krypton have been measured as 1:100.

Now that the energy diagrams are known for both krypton and cadmium it is possible to compare the relative positions of the atomic energy levels concerned in the production of standard wave lengths in the two spectra. The largest term [41] (lowest energy, normal state) of neutral cadmium is $^1S=72{,}538.8$. The primary standard (6438.4696 A) arises from the term combination $^1P_2-{}^1D_3$; in absolute value $^1P_2=28{,}846.6$ and $^1D_2=13{,}319.2$. These terms are well above the middle of the energy diagram, thus guaranteeing that the line will not be easily absorbed or reversed, and still far enough from the highest levels to protect it from large pressure or "Stark" effects. Assuming that the depression of terms observed by Babcock [42] in the iron spectrum applies also to cadmium we may estimate a depression of about 0.013 cm $^{-1}$ for $^1P_2$ and 0.033 cm $^{-1}$ for $^1D_3$ as the pressure changes from 0 to 1 atmosphere. The vapor pressure in a standard Cd tube is usually very small, but even if it should reach 0.1 atmosphere, it would increase the wave length only about 1 part in 8,000,000 or 10,000,000.

Now it is interesting to note that the krypton lines which have been suggested as standards involve the four s-terms (ca 30,000) and ten p-terms (ca 18,000) which occupy roughly the same relative position in the krypton diagram as the above-mentioned cadmium terms in the cadmium diagram. Excepting the lines connected with the long-lived metastable levels s_3 and s_5, the remaining combinations may be expected to be no more sensitive to reversal and pressure effects than the cadmium standard itself.

Other things being equal the yellow line appears to be the best krypton standard.

Unfortunately the theory of hyperfine structure has not been developed far enough to predict what may be expected for krypton lines, and since the existing data which bear on this point are contradictory, it will be necessary to investigate this phase more carefully.

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[41] Fowler, Report on Series in Line Spectra, Fleetway Press, London; 1922.
[42] Babcock, Astrophys. J., 67, p. 240; 1928.