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MEASUREMENT OF "OPTICAL" TRANSITION PROBABILITIES IN THE SILVER ATOM *)

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Synopsis

For 22 spectral lines of the silver atom the probability of spontaneous transition has been derived from measurements of the emission intensity of the line and the population of the corresponding upper level. The medium of excitation was the column of a vertical arc discharge in air of atmospheric pressure. The upper electrode (cathode) was a vertical carbon rod; the lower electrode was either a carbon rod filled with a mixture containing silver, or a silver rod. The length of the arc was 1½ cm, the current ca. 5 A and the axial field strength ca. 30 V/cm. The spectrum of the arc showed cyanogen bands and silver lines, the intensities of which were measured photographically. The arc temperature was derived from intensity ratios of the CN bands; in most cases the temperature was 5000 to 6000°K. For every exposure the relative populations of the upper levels of the silver lines were derived from the temperature. From these populations and the measured intensities of the silver lines the relative transition probabilities of the lines were calculated. The results are compiled in table I. As the concentration of the silver vapour in the arc is not accurately known, reliable values of the absolute transition probabilities cannot be derived from our measurements; we have confined ourselves to a rough estimation. On the other hand it could be established that in the relative measurements there was no disturbing effect of ionization of the vapour in the arc, nor of self-absorption of the measured silver lines. The transition probabilities of the resonance lines have not been measured.

1. *Purpose and method.* Every spectral line of a gas or a vapour is related to a well-defined transition between two energy levels in the atoms and thus to a well-defined transition probability. Be E_n and E_m the energies of the upper and lower levels of the transition, then the energy of the emitted photon is $E_n - E_m$. Be N_n the number of atoms per cm³ in the upper energy level, then the number of spontaneously emitted photons for the transition $n \rightarrow m$ is $A_{nm}N_n$ sec^{-1} cm^{-3} and their concerted energy is $J_{nm} = A_{nm}N_n(E_n - E_m) = A_{nm}N_n hc/\lambda_{nm}$ ergs sec^{-1} cm^{-3}. The transition probability A_{nm} is a constant proper to the spectral line just like the wavelength λ_{nm}. This investigation was aimed at determining the numerical values of the transition probabilities A of the spectral lines of silver vapour

*) Abridged contents of thesis [1]), with addition.

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(or at least the ratios of these values) by measuring simultaneously the energies J of the emitted radiation and the population N of the levels.

For this purpose we used an arc discharge in air of atmospheric pressure, to which a slight amount of silver vapour was admixed. In the spectrum of the emitted light the intensities of the silver lines were measured by the photographic microdensitometric method, whilst the population of the levels was calculated from the temperature of the gas in the discharge, which temperature was measured also. The method depends upon the validity of the law of Boltzmann for the population of the levels in the arc and is described and explained in previous papers [2]), so that we can here confine ourselves to experimental particularities.

2. *The arc.* We used a vertical DC arc between two vertical electrodes. The length of the arc during our measurements was 15 mm. The upper electrode, the cathode, was a carbon rod. The lower one was a bored carbon rod filled with salts or (in later experiments) a solid silver rod. At the time of our earlier experiments spectrally pure carbon rods were not available to us. The carbon rods we used as anodes (Conradty Noris, diam. 10 mm) were bored out to a large width (diameter of the hole $7\frac{1}{2}$ mm, see Fig. 1*a*) so that the remaining thin carbon wall introduced but a small amount of impurities into the arc. The borehole in the anode was filled with a mixture composed of carbon powder ("Norit"), Li_2CO_3 and AgCl, in a weight proportion of 100 : 10 : 1. In later experiments a proportion of 30 : 3 : 1 was used to obtain intenser spectral lines, and finally we used a proportion of 30 : 0 : 1 (no Li-salt) to obtain a higher temperature in the arc. The arc current was 5 amps. In order to be able to measure the weaker Ag lines we raised the partial Ag vapour pressure in the arc further by replacing the filled anode by a silver rod (diam. 4 mm; the lower side of the rod was forced in a big brass block to promote cooling; see Fig. 1*b*). The cathode was a carbon rod 8 mm in diameter. The arc current used was $4\frac{1}{2}$ amps now; at higher currents the electrode melted away. The voltage drop across the electrodes turned out to be 65 volts for both arcs. The arc was connected to a 440 volt DC supply, in series with a resistance. With this high total voltage and with the natural convection of the air in and near the arc the latter was sufficiently stable, so that no special stabilization means were required.

3. *Measurement of the spectral intensities.* From a photographic comparison between the spectrum of the arc and the spectrum of a calibrated tungsten strip lamp the intensities in the spectrum of the arc could be derived. The images of the arc and the tungsten strip were alternatively projected by means of a quartz-fluorite lens onto the slit of a quartz-spectrograph (Hilger E1 large). As a rule some 20 strip lamp spectra (at various currents) were taken on one photographic plate while some arc spectra were admitted in

between through the same width of slit, in order to obtain a correct marking of the wavelength in the strip lamp spectra. The time of exposure varied from 6 to 20 seconds; however, corresponding spectra of arc and strip lamp were exposed exactly the same time. The photographic densities were determined with the same microdensitometer. For every plate used the relation between light intensity and photographic density was derived from the strip lamp spectra and plotted for every wavelength needed; the resulting curves were mutually checked (see page 22 in the thesis[1])). The lines and bands in the

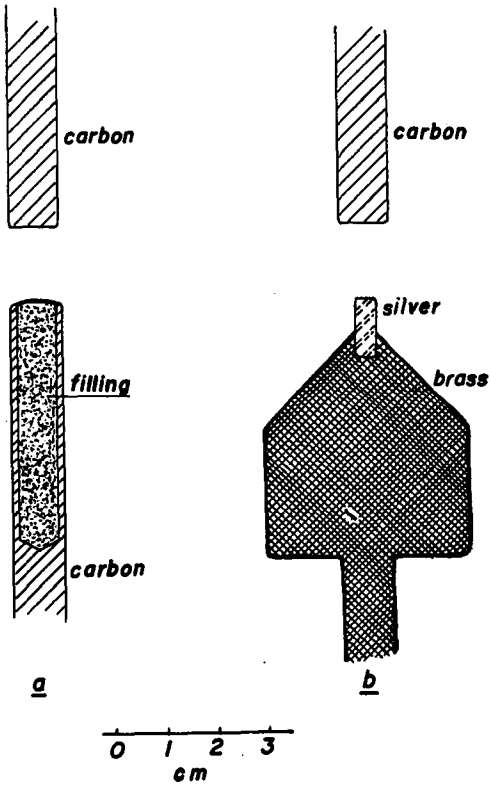

Fig. 1. Electrodes of the arc.
a. Anode = carbon rod with a core containing silver.
b. Anode = silver rod (in brass base).

arc spectra were all measured at the same heigth in the spectrum, viz. the height corresponding to the centre of the arc (7 or 8 mm over the top of the anode). They were measured in the direction of dispersion and their resulting density profiles were converted into intensity profiles using the strip lamp data (see, e.g. fig. 7). The area under the intensity profile, corrected for the effects of the background and of decreasing dispersion of the spectrograph, gives the desired intensity of the spectral line.

In order to obtain simultaneously on the photographic plate weak spectral

lines and strong lines both of moderate density, the upper part of the spectrum was artificially attenuated in the exposures using the silver anode. For this purpose a small plate of fused quartz onto whose lower part a thin platinum film had been vaporized, was placed right in front of the slit of the spectrograph. The transmission factor of the film, determined by means of strip lamp spectra, showed a slight increase from 0.15 at 5200 Å to 0.19 at 3600 Å. The silver spectra photographed in this way were measured with the microdensitometer just over and under the transition between the attenuated and the unattenuated parts; the results obtained for the attenuated parts were corrected by dividing them by the transmission factor of the platinum film.

In order to make the background and the (broad) wings of the spectral lines sufficiently measurable, the photographic plates were as a rule preexposed to an amount of light just above the threshold value of the emulsion. In the arc spectrum the formation of the background is partly (and in the strip lamp spectra wholly) due to the reflection or scattering of light in the spectrograph. This effect could be detected from the density occurring on the plate over and under the spectrum (see thesis [1]) p. 17). It could be counteracted to some extent by the use of a diaphragm (see Van Hengstum[2]) page 92 sub 6*a*). A spectral line can be corrected for this and other continuous background effects by subtracting the intensities, the intensity of the background being deduced from the spectrum just to the left and to the right of the spectral line (interpolation). For the other part, the background in the arc spectrum results from undesirable spectral lines and molecular bands of the arc vapour. We shall revert to the correction for this background effect in our discussion of particulars of the measurements (sections 6 and 7).

4. *The determination of the temperature of the arc.* The temperature of the arc was determined from the CN bands which were always present in the spectrum. The photographed bands were traced with the microdensitometer in the direction of dispersion. The recorded density profile was transformed into an intensity profile. In one of the band sequences the profile areas of the first and second bands were determined, always up to the place where the next band started; from the results the background value (continuum + + disturbing lines) was subtracted. The ratio of the intensities of the bands determined in this way depends on the temperature of the arc; the relation is quantitatively known from earlier measurements [3]). In this way the arc temperature for each of the silver spectra could be found.

In the spectra obtained with a filled carbon anode the CN bands usually were intense. In this case the temperature was determined from the band sequence $\Delta v = -1$ ($\lambda = 4216$ Å etc.) because this sequence showed a suitable photographic density, as did the silver lines. Unfortunately, the measurement of the band 4216 Å was rendered difficult by the silver lines 4211 Å and 4213 Å lying within this band, near to the head. In the spectra

obtained with the silver anode the CN bands were weaker. In this case the density of the sequence $\Delta v = 0$ ($\lambda = 3883$ Å etc.) turned out to be more suitable for the determination of the temperature. Moreover this sequence offers the advantage that the ratio of the measured intensities is less sensitive to possible errors in the estimation of the continuous background (which estimation is founded upon a somewhat problematic extrapolation). For full particulars see pp. 26–28 of the thesis [1]).

5. *Checking measurements.* We had to verify the negligibility of three possible sources of errors, also discussed by Van Hengstum[2]).

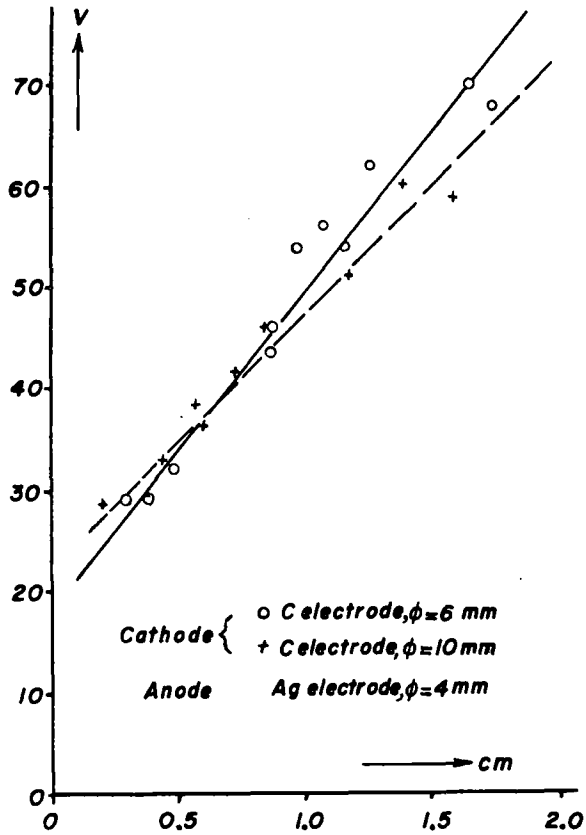

Fig. 2. Relation between the potential difference (volts) of the electrodes and the length (cm) of the arc, at constant current ($4\frac{1}{2}$ A).

a) The electric field between the electrodes is a possible source of errors because it effects an extra supply of energy to the free electrons in the arc. As a result the electron "temperature" is higher than the gas temperature which will cause deviations from the Boltzmann formula we used in determining the population of the energy levels. For a type of arcs produced with

copper electrodes Van Lingen [4]) mentions such deviations. In our silver arcs, however, the field strength proved to be rather low, viz. about 30 volts/cm: see fig. 2. Experience has shown and theory makes it acceptable that in such cases this source of errors may be neglected.

b) Strong ionization of the silver vapour in the arc also might lead to measuring errors. Naturally, the degree of ionization would then be highest in the hot central part of the arc, and the measured spectrum of the silver atoms would have been radiated mainly from the cooler outer parts of the arc. The CN radiation, however, is emitted mainly from the central part of the arc, so that the temperature, derived from the CN bands, holds for that part. Our

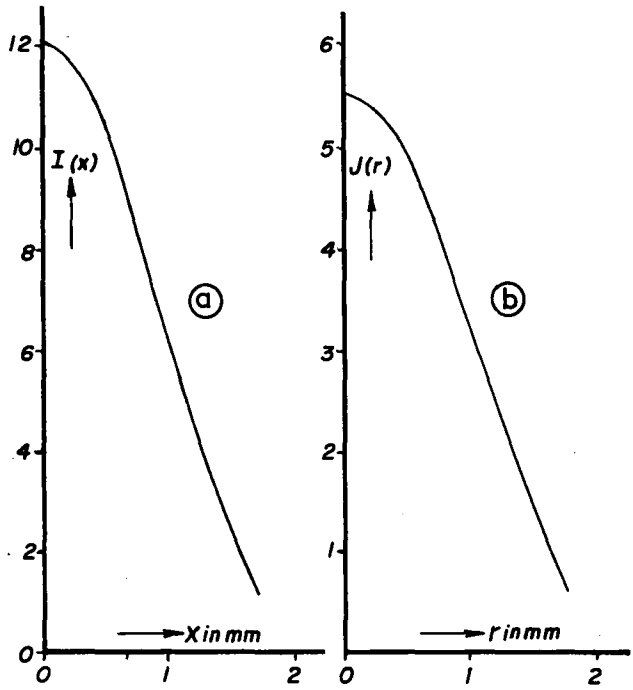

Fig. 3. Radial fall of the emission of a silver line in an arc with silver anode.
a. Intensity distribution across the projected image of the arc, measured for $\lambda = 3982$ Å.
x = distance to the central axis of the image of the arc.
b. Radial fall of the production of 3982 Å per cm³ of the arc gas, derived from fig. 3*a*.
r = distance to the central axis of the arc.

calculation of the transition probabilities from the intensities of the atomic lines would then have been based upon too high temperatures. From spectra obtained with the slit of the spectrograph placed perpendicular to the axis of the arc it was found that the silver spectrum is radiated chiefly from the central part of the arc; see fig. 3. It was also found that the radial temperature gradient in the central part of the arc was only small, see fig. 4.

c) Self-absorption is the third threat to the correctness of our results. As

it was our aim to determine the probabilities of spontaneous light emission it was inadmissible for the stimulated emission and the self-absorption in the arc discharge to have more than a negligible influence on the measured intensities of the silver lines. In checking this we could confine ourselves to self-absorption, as the absorbed photons outnumber by far the photons due to stimulated emission. Their ratio is $\exp(-h\nu/kT)$, where ν is the frequency of the spectral line and T is the temperature of the gas; in our case this ratio was always smaller than 2%. Theoretically one can derive that in a gas having a temperature T the self-absorption of a spectral line with a wavelength λ may be neglected, if the true intensity I_m of the peak of the line is small as compared with the intensity I_z of a black body of the same temper-

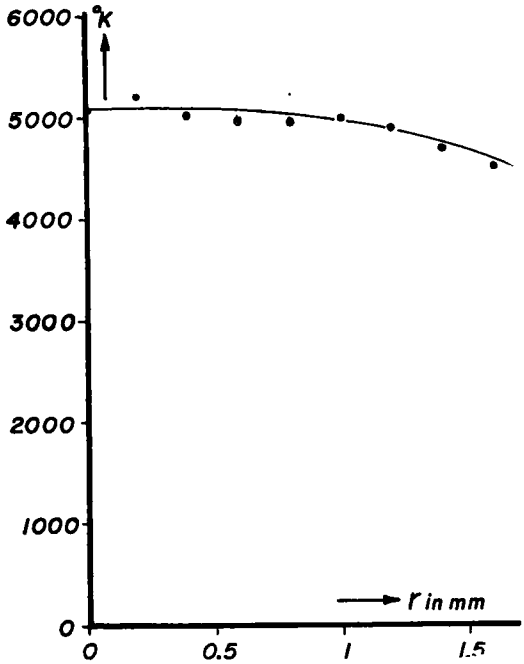

Fig. 4. Radial fall of the temperature in an arc with silver anode.
The radial fall $J(r)$ of the light production was determined for the CN bands $\lambda =$ $= 3883$ Å and 3871 Å (analogous to fig. 3*b*). From their ratio the temperature corresponding to every r value was derived.

ature T at the same wavelength λ. As was evident from absolute intensity measurements the ratio I_m/I_z for the strong line $\lambda = 5209$ Å in our experiments with the silver anode was only ca. 1% which means that the self-absorption is, indeed, negligible. In our photographs this line had a width of about 2 Å, while the widening due to the apparatus was about 1 Å (as derived from some near-by iron lines); consequently the resolving power was sufficient for deriving approximately the true intensity of the peak I_m from

the measured intensity profile of the line. However, with some other silver lines the measured width of the line profile was nearly equal to the widening caused by the spectral apparatus; here the true profile width was possibly much smaller and the true peak-intensity I_m accordingly much larger than in the measured profile. If we suppose that the true width is determined by the Doppler-effect and by "classical" collision-damping we actually find values much smaller than the width caused by the apparatus. When we divide the measured total intensity by the small true line width we nevertheless find for these narrow lines $I_m \ll I_z$, which result again points to negligible self-absorption. A more exact calculation and the numerical results obtained are described in the thesis[1]).

6. *Measurements with the filled carbon anode.* The measurements with arcs between carbon electrodes in which the anode was filled with, inter alia, a silver salt, concerned a number of rather strong lines in the spectrum of the silver atom. The relative gA values of the lines obtained (g = the statistical weight of the upper level, A = the transition probability of the line) are compiled in column 4 of Table I. We shall now describe experimental particularities of the individual lines.

The intensities of the lines of the group under consideration were all measured relative to the intensity of the line $\lambda = 5209$ Å, as this line was particularly well measurable. In the photographs of this group the line 5209 Å appeared to have a moderate and therefore well-measurable density and the spectral background near 5209 Å showed but few irregularities.

From the spectrum we learned that the arc was contaminated by titanium and iron. The Ti line 4667.6 Å partly coincided with the Ag line 4668.5 Å. The intensity of the Ti line alone could be derived from the intensities of the Ti lines 4682 Å and 4656 Å (measurable in our spectrum), using the known ratio *). Bij subtraction the intensity of the Ag line was then found. This line, 4668.5 Å, is the stronger component of the second doublet of the sharp series. The weaker component of the same doublet, 4476 Å, was difficult to measure as it was superimposed on the tail of the CN sequence $\lambda = 4607$ Å etc., a rather undulating intensity profile resulting from the rotation-line structure; see fig. 5*a*. Therefore spectra were taken also from the same type of arc but with an anode filling not containing the silver salt. The logarith-

*) The Ti lines $\lambda = 4682$ Å, 4668 Å and 4656 Å mentioned above have the same upper level. The ratio of their intensities is therefore indifferent to the conditions of excitation. In our arc without silver we found for the ratio of these intensities 178 : 140 : 100. From several measurements on the Ti lines just mentioned Van Stekelenburg [5]) found the ratio 170 : 145 : 100.

We should remark that the Ti line 5210 Å, although about twice as strong as the Ti line 4668 Å [5]), interfered only slightly with the measurement of the Ag line 5209 Å, as the latter was about 17 times as strong as the Ag line 4668 Å. Consequently, the correction is only small.

The Ti line 3982 Å did not influence the measurement of the Ag line 3982 Å. The titanium was contained as an impurity in the carbon-powder of the anode filling and this Ag line was measured only in arcs with a solid silver anode.

mically plotted intensity profiles outside the line were made to coincide as best possible by shifting them vertically (fig. 5*a*). The net intensity profile of the Ag line was obtained by subtraction (fig. 5*b*).

Of the first compound doublet in the diffuse series, the weak third component (satellite) 5472 Å could be measured in a few spectra, in addition to the main components 5209 Å (already mentioned) and 5466 Å. The measurement of 5472 Å was difficult owing to the background, which comprised the broad wing of the stronger component 5466 Å.

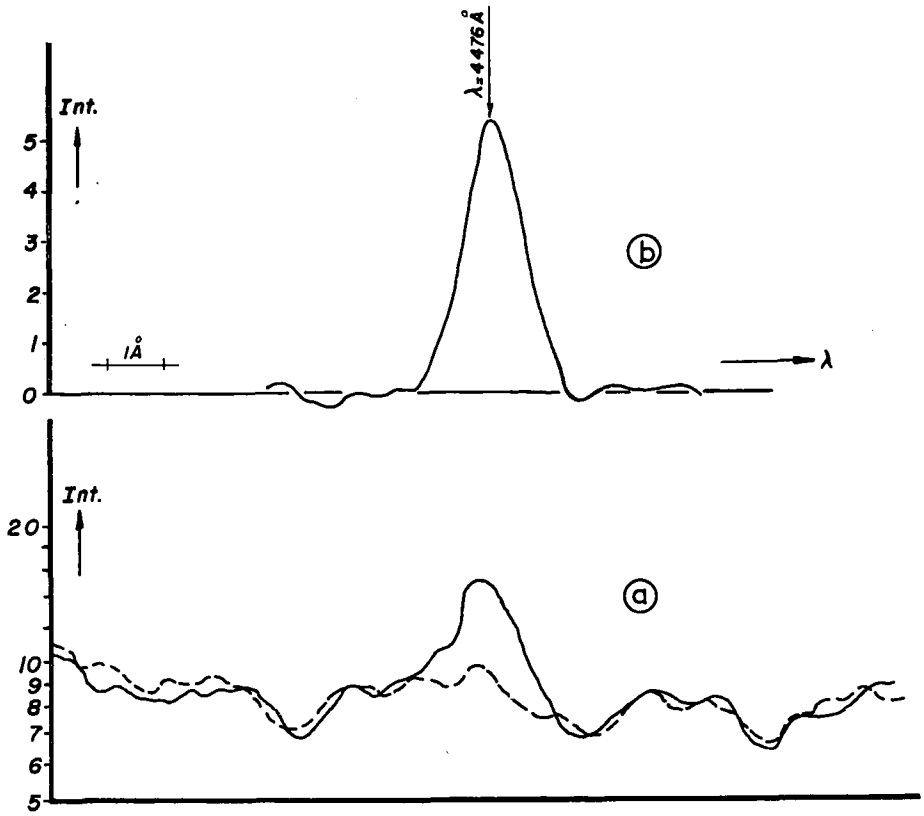

Fig. 5. Intensity profile of the silver line 4476 Å.

a. Drawn curve = intensity near 4476 Å, measured in the arc spectrum. Dashed curve = do., for an arc not containing silver. The parts of the curves outside the silver line are made to coincide as best possible.

b. Profile of the silver line (on a linear scale) resulting from the difference of the two profiles in fig. 5*a*.

In the second compound doublet the strongest component 4211 Å lies in the CN band 4216 Å, very close to the band head. Therefore the intensity profile was compared with that of spectra without silver, obtained from arcs with the same temperature (and hence the same profile of the band). By

graphic subtraction (by the method mentioned above for the line 4476 Å) the net profile of the line 4211 Å was found (see fig. 11 in the thesis [1])). Even with this graphic method the weak satellite, situated quite near, could not be measured with any degree of accuracy. The component 4055 Å was so situated in the tail of the band sequence $\lambda = 4216$ Å etc. that here again the method of graphic subtraction had to be applied (see fig. 12 in the thesis [1]).

The arc temperatures in the measurements mentioned above for the lines 4668 Å and 4476 Å, were between 5000°K and 5500°K. In the measurements of the lines 5466 Å and 5472 Å the temperature was of less importance, as the upper levels of these lines and the reference line 5209 Å are almost equally high. In the measurements of 4211 Å and 4055 Å the temperature turned out to range from 3800 °K to 5500 °K.

7. *Measurements with the silver anode.* Several silver lines which in the exposures with the filled carbon anode were too weak to be measured, appeared to contrast sufficiently with the background in exposures with the silver anode. As the time of exposure was adapted to the new lines, the lines which were already measured became too dense in these photographs; however, some of the strong lines were measurable in the artificially attenuated part of the spectrum (see section 3). The relative gA values of the lines produced by means of the silver anode are compiled in column 5 of table I.

In the measurements of the intensities the other lines of the group in question were compared with the line 3982 Å, as this line was very well measurable, just like 5209 Å in the former group.

The lines 4668 Å and 4476 Å, already mentioned in section 6, were measurable in the attenuated part and the reference line 3982 Å could be measured in the unattenuated part of the same spectrum.

The next doublet of the series consists of the line 3841 Å and the (reference) line 3982 Å. The determination of the ratio of their intensities was made difficult by the irregularly undulating background originating from the CN band sequence $\lambda = 3883$ Å etc. By the method of graphic subtraction described in section 6 (for the line 4476 Å) the net profile of the line 3841 Å could be determined (see fig. 13 in the thesis [1])). The silver-free spectrum needed in this method had been obtained from an arc with a copper anode.

The stronger component 3709 Å of the next doublet showed rather a smooth background, so that, as a rule, a simple correction by interpolation was sufficient. The component 3587 Å, however, was partly situated on the steep slope of the second head of the CN band sequence $\lambda = 3590$ Å etc. Here again we had to use the graphic method; see fig. 6. Just as in the case of the line 4211 Å the profile of the background had to be derived from the spectrum of an arc containing no silver and having almost the same temperature as the arc in question.

The measurement of the stronger line 3570 Å of the next doublet was

hampered by the Fe line 3570 Å. The procedure applied is the same as described in the case of the Ag line 4668.5 Å. The intensity of the Fe line alone could be determined from the intensity of the Fe line 3565 Å *) which was measurable in the photographs. By subtraction the intensity of the Ag line could be derived. The measurement was not very exact, as the unwanted

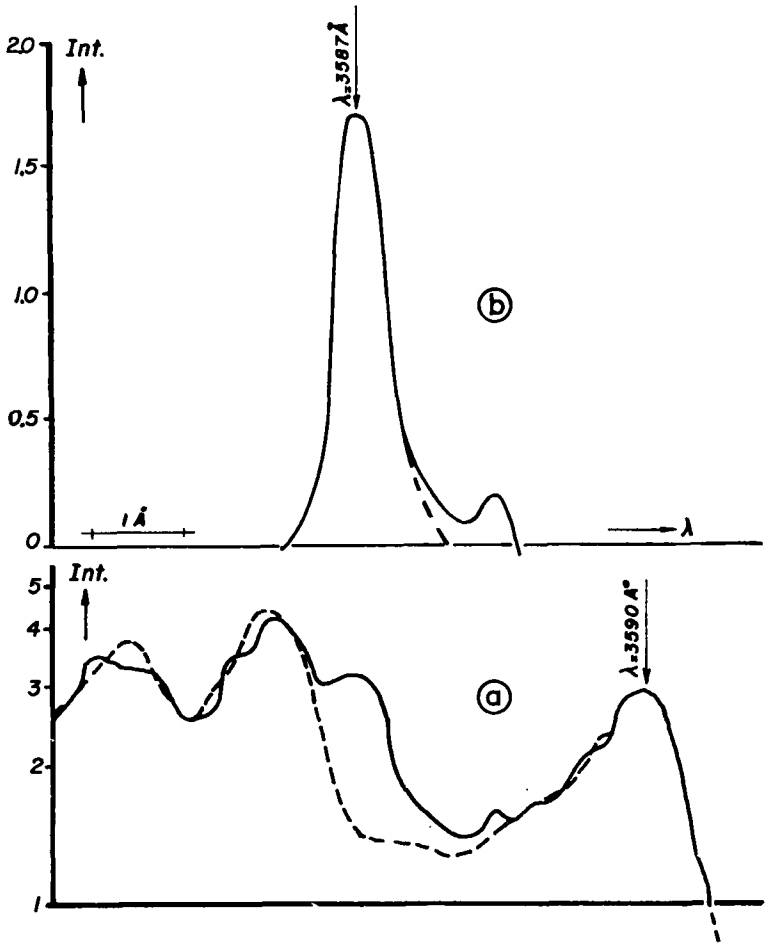

Fig. 6. Intensity profile of the silver line 3587 Å. Meaning of the curves the same as in fig. 5.

Fe line was almost as strong as the desired Ag line. The other component of this doublet could not be measured, as its wavelength 3456 Å differs only little from the wavelength of the stronger and broad Ag line 3457 Å of the diffuse series.

The strong component 3488 Å of the next doublet is the last of the sharp

*) Measurements of the Fe lines 3570 Å and 3565 Å in the spectrum of the arc containing no silver resulted in a ratio of intensities 26 : 10.

series that has been measured. The line rose only little over the background which showed irregular fluctuations. The other component 3435 Å could not be measured, owing to the proximity of the very strong and broad resonance lines of silver. Neither could the other lines of the sharp series be measured with any precision.

Concerning the diffuse series it has to be emphasized that the lines in the arc spectrum are indeed diffuse, i.e. broad. This applies particularly to the higher numbers of the series now to be discussed. For this reason it was impossible to measure separately the weakest component of any of these compound doublets; the extended wing of the near stronger component covered the weak satellite almost completely; as a rule these components were measured together.

The diffuse line 5209 Å already considered in section 6 was measurable in the attenuated part, the line 3982 Å in the unattenuated part of the same spectrum. Its partner 5466 Å and the lines 4211 Å and 4055 Å of the second compound doublet, the measurements of which are described also in section 6, showed too high a density in this case.

Of the next compound doublet the strongest component 3811 Å was measurable only in the attenuated part of the spectrum *). The background consisted mainly of the tail of the CN band sequence $\lambda = 3883$ Å etc., but was much weaker than the line and showed regular undulation; by simple interpolation it could be drawn with sufficient accuracy into the profile of the line (see fig. 7). The other component 3683 Å had a smooth background.

Both the components 3625 Å and 3508 Å of the next compound doublet were well measurable. The background was almost smooth in the case of 3625 Å and showed only a few weak undulations in the case of 3508 Å.

The components 3521 Å and 3411 Å of the next compound doublet were also measurable, but rather weak. The background at 3521 Å was nearly flat and at 3411 Å regularly inclined on account of the extended wing of the resonance line 3383 Å.

The last line measured in the diffuse series is the strong component 3457 Å of the next doublet. This line could not be separated on our photographs from the line 3456 Å of the sharp series. From the measured intensity of the line 3570 Å we estimated the intensity of its partner 3456 Å, assuming that the ratio of the gA values of doublet lines is the theoretical ratio 2 : 1. By subtraction we could derive the net intensity of 3457 Å; this intensity proved much larger than the intensity of 3456 Å.

The remaining lines of the diffuse series could not be measured with any accuracy. This is caused by their hazy character and also – as in the case of the sharp series – by the circumstance that the limit of this series lies at

*) This line was also produced by the arc with filled carbon anode (section 6). However, it was not measurable there because of the strong CN background.

a somewhat lower wavelength (3169 Å) than the resonance lines (3383 Å and 3281 Å), so that the lines with high quantum numbers are situated on both sides of and between the resonance lines, and are covered by the very extended wings of these lines.

The temperatures in the measurements mentioned in this section were between 5300°K and 5700°K.

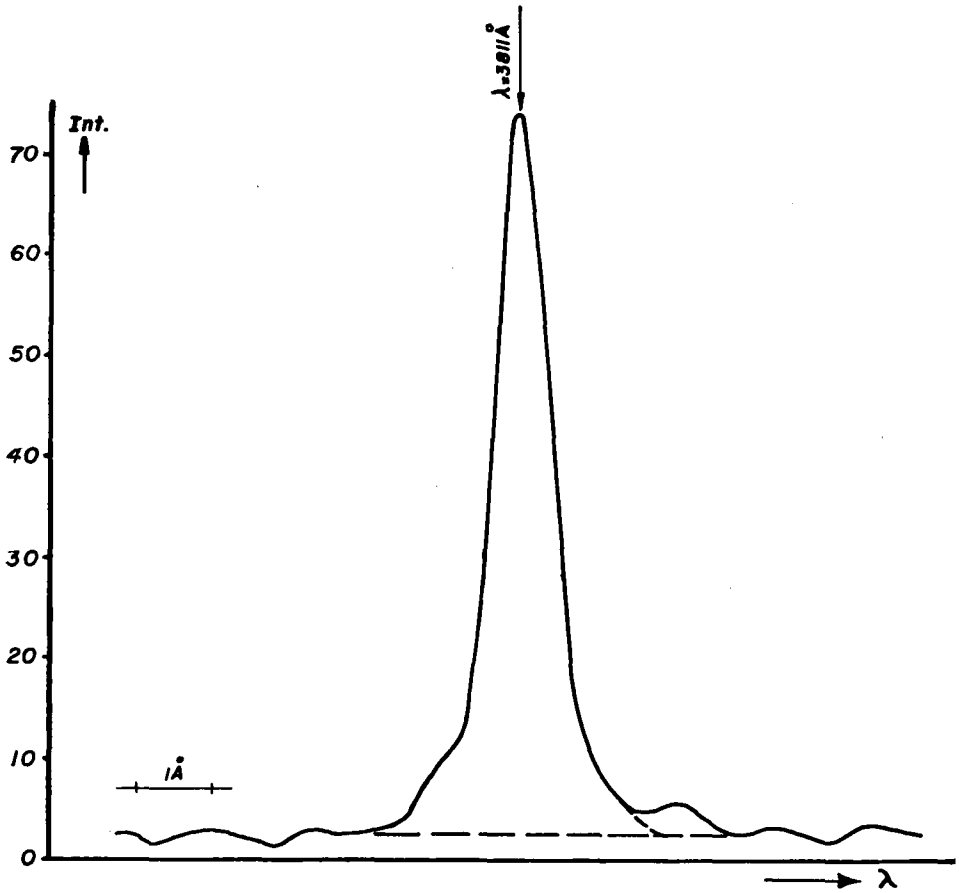

Fig. 7. Intensity profile of the silver line 3811 Å. The background under the line has been interpolated, because a blank exposure (without silver) showed no peculiarities at this wavelength.

8. *Survey of the results.* For every eligible photograph of the arc spectrum the measured density profiles of the CN bands and the Ag lines were transformed into intensity profiles. From the intensity ratio of the bands the temperature of the arc which produced the spectrum could then be derived. From this temperature and the relative intensities of the lines (areas under the profiles) the relative gA values of the lines resulted. This was done with each exposure. Next, the results of several exposures were averaged for

every line (measured in regard to a reference line). Table I gives a compilation of the mean values determined in this way. Column 4 relates to the measurements made with a filled carbon anode (reference line: 5209 Å), discussed in section 6. Column 5 relates to the measurements made with a silver

TABLE I

Measured relative gA values of silver lines										
1	2	3	4a	4b	4c	5a	5b	5c	6	7
Transition	Upper level	Wave-length	Measurements I			Measurements II			Result	Syst.
			$gA_{rel.}$	± %	m	$gA_{rel.}$	± %	m	$gA_{rel.}$	%
$6^2S_{1/2}$—$5^2P_{3/2}$	5.256	8273.52	0.107		(1)				4.3	
$6^2S_{1/2}$—$5^2P_{1/2}$	5.256	7687.78	0.069		(1)				2.8	
$7^2S_{1/2}$—$5^2P_{3/2}$	6.405	4668.48	0.083_5	$2._5$	30	3.65	$1._5$	9	3.5	$6._5$
$7^2S_{1/2}$—$5^2P_{1/2}$	6.405	4476.04	0.045	$1._5$	28	1.83	3	9	1.82	$6._5$
$8^2S_{1/2}$—$5^2P_{3/2}$	6.872	3981.58				1.00	(reference)		1.00	0
$8^2S_{1/2}$—$5^2P_{1/2}$	6.872	3840.75				0.55	3	40	0.55	5
$9^2S_{1/2}$—$5^2P_{3/2}$	7.086	3709.20				0.48	$2._5$	44	0.48	$5._5$
$9^2S_{1/2}$—$5^2P_{1/2}$	7.086	3586.67				0.24_5	3	36	0.24_5	$5._5$
$10^2S_{1/2}$—$5^2P_{3/2}$	7.217	3569.72				0.21	3	14	0.21	6
$10^2S_{1/2}$—$5^2P_{1/2}$	7.217	3456.10				—			—	
$11^2S_{1/2}$—$5^2P_{3/2}$	7.298	3487.79				0.10_5	4	4	0.10_5	$6._5$
$5^2D_{3/2}$—$5^2P_{3/2}$	6.015	5471.55	0.18_5	7	24				7.4	$9._5$
$5^2D_{5/2}$—$5^2P_{3/2}$	6.018	5465.50	1.65	1	61				66	$9._5$
$5^2D_{3/2}$—$5^2P_{1/2}$	6.015	5209.08	1.00	(reference)		$37._5$	$3._5$	9	40	9
$6^2D_{3/2}$—$5^2P_{3/2}$	6.690	4212.82	—						—	
$6^2D_{5/2}$—$5^2P_{3/2}$	6.691	4210.96	0.44	5	36				17.7	5
$6^2D_{3/2}$—$5^2P_{1/2}$	6.690	4055.48	0.24	3	30				9.7	5
$7^2D_{3/2}$—$5^2P_{3/2}$	6.997	3811.78 }				8.3	4	9	8.3	5
$7^2D_{5/2}$—$5^2P_{3/2}$	6.998	3810.94 }								
$7^2D_{3/2}$—$5^2P_{1/2}$	6.997	3682.51				4.9	2	41	4.9	$5._5$
$8^2D_{5/2}$—$5^2P_{3/2}$	7.165	3624.68				4.1	2	44	4.1	6
$8^2D_{3/2}$—$5^2P_{1/2}$	7.164	3508.03				2.1	3	44	2.1	6
$9^2D_{5/2}$—$5^2P_{3/2}$	7.267	3521.12				2.2_5	$1._5$	44	2.2_5	$6._5$
$9^2D_{3/2}$—$5^2P_{1/2}$	7.267	3410.79				1.5_5	7	9	1.5_5	$6._5$
$10^2D_{5/2}$—$5^2P_{3/2}$	7.323	3457.07				1.2	5	14	1.2	$6._5$

2 = energy of the upper level (eV) } comp. A.G. Shenstone,
3 = wavelength of the line (Å) } Phys. Rev. **57** (1940) 894.
4a = mean value of gA_{line}/gA_{5209} } measurements with silver-filled
4b = accidental error in the mean value } carbon anode.
4c = number of measurements (exposures) } measurements with silver-filled carbon anode.
5a = mean value of gA_{line}/gA_{3982} } measurements with silver anode.
5b and 5c: see 4b and 4c. } measurements with silver anode.
6 = the same as 5a, combined with converted values from 4a.
7 = estimated systematic error (comp. section 9).

anode (reference line: 3982 Å), discussed in section 7. Column 6 combines columns 4 and 5; the link is formed by the lines 5209 Å, 4668 Å and 4476 Å, measured in both types of arcs. For making this column the relative gA values of column 4 were all multiplied by 40.3. In this way the relative gA

values of the three lines just mentioned were adapted as best possible to the relative gA values of column 5 (apparently the factor 40.3 is the ratio of the gA values of the two reference lines).

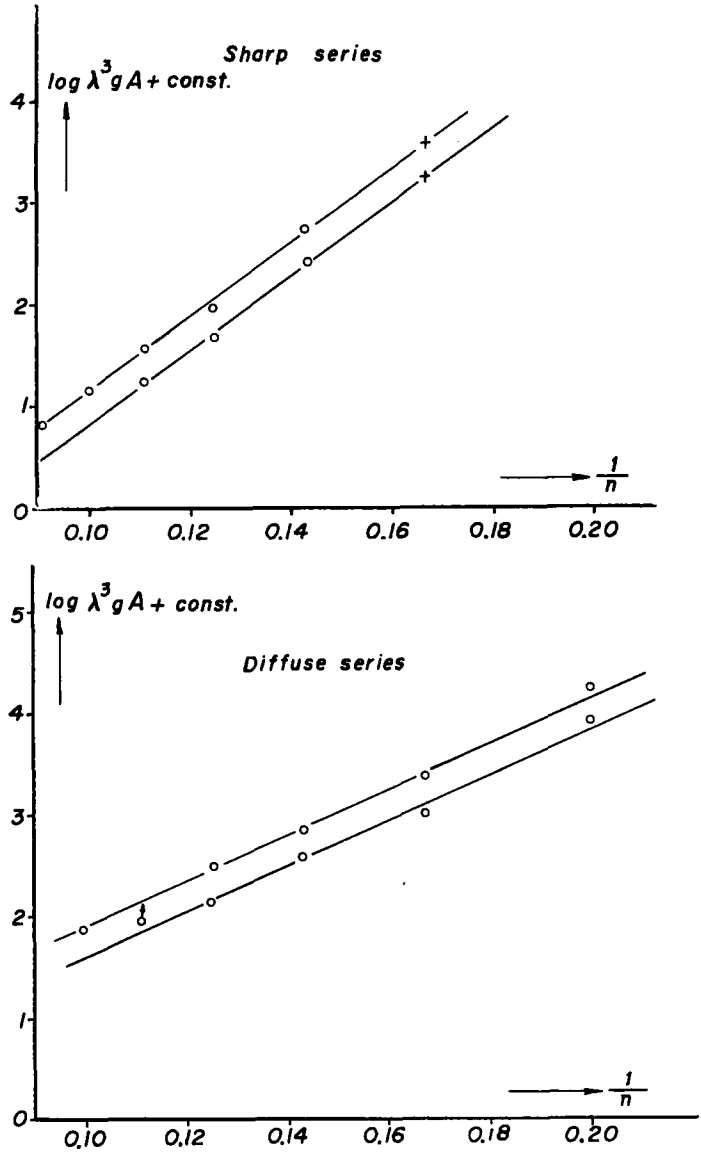

Fig. 8. Linear relation between log $\lambda^3 gA$ and $1/n$ (n being the principal quantum number of the upper level). The crosses represent the infrared lines.

Figure 8 shows that according to the measurements there exists both in the sharp and in the diffuse series a linear relation between log $\lambda^3 gA$, computed from table I column 6, and $1/n$ (n is the principal quantum number). This

empirical relation has also been found for the sharp series of the alkaline elements (theorem 1*a* of the thesis[1])); in this case the slopes of the resulting straight graphs show the same proportion as the numbers of the rows of the periodic system (theorem 1*c*) so 2 : 3 : 4 : 6: 8 for Li, Na, K, Rb and Cs respectively.

The infrared first doublet of the sharp series of silver was measured not by us but by Van Langen [6]). From measurements on a carbon arc, the lower electrode of which was filled with 10% $AgNO_3$ in carbon powder, he derived the ratios of intensities $I_{8274}/I_{5209} = 0.27$ and $I_{7688}/I_{5209} = 0.19$*). The temperature of the arc, derived from the intensity ratio of the band heads in the CN band sequence $\Delta v = -2$ ($\lambda = 4607$ Å etc.) turned out to be 6000°K. It follows that the ratio $gA_{8274}/gA_{5209} = 0.099$ and $gA_{7688}/gA_{5209} = 0.065$. Though this result is based on only one measurement it fits in well with the straight graphs of fig. 8.

As can be seen from fig. 8, the ratio of the intensities of the doublet components does not show a systematic increase or decrease with the principal quantum number n. Table II lists the values; for the compound doublets in the diffuse series the satellite is added to the strongest component, so that the resulting ratio "theoretically" ought to have the value 2. It is hard to say if the irregular deviations from 2.00 in tabel II are real or are mainly a result of systematic errors in our measurements. The spectral backgrounds of the various lines differ in structure; the systematic errors resulting from this background may consequently be opposed in sign and differ in value for the various doublets and compound doublets.

TABLE II

Doublet ratios			
Components (λ, Å)		$\frac{(gA)_a}{(gA)_b}$	$\frac{(\lambda^3 gA)_a}{(\lambda^3 gA)_b}$
a	b		
8274	7688	1.56	1.84
4668	4476	1.90	2.03
3982	3841	1.83	2.03
3709	3587	1.98	2.15
5472 + 5466	5209	1.81	2.14
4213 + 4211	4055	2.04	2.29
3812 + 3811	3683	1.70	1.90
3625	3508	1.98	2.18
3521	3411	1.47	1.61

Remark: Errors of 3–7 per cent in the measured doublet ratios are probable; see table I. The systematic errors, mentioned in section 9 sub *b* and *c*, do not affect the ratio.

9. *Discussion of errors.* We can distinguish between accidental errors, whose real values can be derived from the spread of the measuring results,

*) The reciprocal value 16.7, mentioned in the thesis, has to be divided by the ratio of dispersion.

and systematic errors, which we shall try to estimate by a critical discussion of the measuring method.

In table I each of the gA values is the mean ($\bar{u}$) of the results (u) of a number (m) of exposures. Be Δ the root-mean-square of the deviation $u - \bar{u}$, and δ the root-mean-square error in the final result $\bar{u}$, then

$$\Delta = \sqrt{\sum(u - \bar{u})^2}/\sqrt{m - 1} \text{ and } \delta = \Delta/\sqrt{m}.$$

The columns 4 and 5 of the table give, in addition to the gA value of each silver line, the accidental error δ calculated in this way and the number of exposures m. For most lines m is so high that δ is much smaller than Δ, which means that the accidental errors in the individual exposures are "averaged out". Increasing the number of exposures is then of no use as, mostly, δ is already smaller than the expected systematic error.

In order to account for the accidental errors and estimate the systematic ones we will discuss the measuring method.

a) The photographic measurement of the spectral lines introduces accidental errors owing to the graininess of the photographic plate and also to the differences in sensibility of the various parts of the sensitive layer. Further systematic errors are introduced owing to the Eberhard-effect, which errors depend on the intensity and the width of the line. For some lines the accidental error was enlarged because a large amount of background had to be subtracted. Moreover, a systematic error sometimes will arise from a systematically wrong drawing of the background in the line profile. When we estimate and summarize quadratically the accidental errors just mentioned for the case of a reasonably favourable line/background ratio, the contribution to the accidental error in the measured intensity of a line is about 7% per exposure, so in the ratio of intensities of two lines it is about $7\sqrt{2} = 10\%$ per exposure and in the mean value of m exposures about $10/\sqrt{m}$ %. The corresponding three values for the systematic error are 3 or 4%, 5% and 5%; the systematic error is not influenced by the number of exposures.

b) In deriving the intensities from the densities we used strip lamp spectra. The photographic errors mentioned under *a* are smaller in strip lamp spectra than in spectral lines, the first being wider and having less background. Especially when using old strip lamps with cylindrical bulb one has to be aware of possible errors introduced by a tarnish on the glass envelope absorbing the ultra-violet, by the grooved structure of the strip surface, and by zig-zag reflection between the strip and the envelope; one has to pay attention to the deviations from the calibration of the strip lamp associated with these effects [7]). We have corrected our results for these effects as far as data were available. The amount of the correction is somewhat doubtful, as a result of the incompleteness of these data. Thus our results probably contain a residual error. This error is a function of the wavelength. We estimate it to be about 5%, 3 or 4% and 2 or 3% for lines near 6000 Å,

5000 Å and 3500 Å, respectively, in regard to a line near 4000 Å. Included is a small contribution resulting from inaccuracies in the strip lamp current etc. An increase of the number of the exposures will hardly duce the percentages just mentioned; the errors are for the greater part systematic in nature.

c) The determination of the temperature of the arc also contains a measurement of an intensity ratio viz. of subsequent molecular bands. In this case the errors mentioned sub *a* and *b* are as a rule small, as the bands to be compared are rather wide, have almost the same profiles and are near to each other in the spectrum. Only the correction for the background is somewhat doubtful, as it is largely based on the extrapolation of the backgound measured just in front of the first head of the sequence. A probably more serious error arises from the uncertainties in the relation between the measured intensity ratio of the bands and the arc temperature. In addition to an accidental error of about 100° per exposure we believe to have to take into account a systematical error of about 200°. The latter estimation is not very reliable and a nearer investigation is wanted. The influence of an error in the temperature upon the ratio of the gA values of two lines is proportional to the difference in energy of the upper levels; an error of 200° at 5500°K results in an error of about 8% in the ratio of the gA values at a level difference of one electron-volt.

d) In our ordinary exposures the spectrum was composed of light emitted from the central part and light from the boundary parts of the arc. The temperature of the arc derived from such an exposures is a sort of average of the temperatures in the various zones of the arc. A similar consideration holds for the intensity ratios of the silver lines; here, however, a different way of averaging appears (different "weights" of the zones). In practice the difference is of less importance as both the bands and the lines are emitted mainly from the central part of the arc, where the temperature gradient is small; see figs. 7 and 8. A "mean" temperature of 5050°K was found in the case of fig. 8, where from the temperature-curve a maximum (central) temperature of 5100°K can be derived. We believe that the errors introduced by this way of averaging are negligible as compared with the errors already mentioned before. Furthermore we believe the errors due to absorption of light in the cooler outer parts to be negligible as the absolute population of the lower levels of the lines in question is lower in the outer parts than it is in the central part of the arc. See further section 5*c*.

e) As is usual with arcs, the concentration of the (silver) vapour and the temperature fluctuated in time. In the intensity measurement an averaged value is obtained. The averaging of fluctuations in the concentration of the vapour at constant temperature is perfectly admissible in the case of our relative measurements, as the various silver lines are measured simultaneously and their momentary intensities are proportional to the momentary vapour concentration. The averaging of intensities of lines and bands with

regard to fluctuations in the arc temperature is strictly speaking incorrect for reasons analogous to those mentioned sub *d*. In practice, however, the errors thus induced are small for ordinary exposures, in analogy to those discussed sub *d*. They are difficult to estimate. We will neglect these errors.

The values of the errors mentioned sub *a*, *b* and *c* are compiled and explained on page 55 ff of the thesis[1]).

When we add quadratically the estimated values of the accidental errors considered above, and divide by $\sqrt{m}$ (see sub *a*), we find for most of the lines values approximately in accordance with the error percentages found experimentally and compiled in columns 4 and 5 of tabel I. For a few lines with a highly interfering background the percentages found experimentally are naturally larger. In addition to the accidental errors the systematic errors considered above are of importance. As we do not know their signs, and as they are independent of each other, we have to add them quadratically, just like the accidental errors. When we do this with the values considered sub *a*, *b* and *c*, we arrive at the values compiled in the last column of table I. This estimation is somewhat speculative, chiefly on account of the rather arbitrary supposition of a systematical error of 200° in the temperature.

10. *Absolute values.* If the concentration of the silver vapour in the arc were known, the absolute value of the transition probability A of a spectral line could be calculated from the measured emission intensity J, by means of the formula $J = ANhc/\lambda$ (viz. section 1). We have no method for an accurate calculation of the concentration of the silver vapour but we will try to estimate this concentration in two ways (cf. Van Stekelenburg [8])) to find at least the order of magnitude of the absolute A values of the lines. As an example we will consider a group of spectra obtained with the silver anode; the temperature in the centre of the arc was about 5700°K (mean value of 9 spectra).

First estimate: based upon the vaporization of the silver electrode. The decrease of the length of the silver rod 0.4 cm in dia. was 1.4×10^{-4} cm/sec or 1.0×10^{18} atoms/sec at a current of 4.5 amps. For our estimate we suppose that this amount of silver vaporizes and that the vapour is dispersed by diffusion from a point source (the top of the anode) in a vertical gas current (convection[9])). Setting aside complications owing to condensation, ionization, thermodiffusion etc., the following relation [8]) holds:
$n/N = 4\pi Dz$; here N = the number of vapour atoms per cm^3 in a point P on the axis of the arc z cm over the source which delivers n atoms per sec. An estimation [1]) of the constant of diffusion for silver atoms in air at 5700°K gives $D = 40$ cm^2/sec*). With $n = 1.0 \times 10^{18}$, $D = 40$ cm^2/sec and $z = 0.75$ cm, the formula leads to $N = 2.7 \times 10^{15}$ atoms(+ ions)/cm^3.

*) The numerical values of D etc. in the thesis [1]) are not correct.

Second estimate: based upon the concentration of the electrons and on the temperature. The temperature of 5700°K in our arc obtained with a silver electrode at 4.5 amps is clearly lower than the temperature of about 6200°K which prevails in a 1.5 cm arc drawn between two carbon electrodes at 4.5 amps [10]). The atoms and molecules which are ionized in the carbon arc and thus carry the current, will be ionized much less strongly at the lower temperature of our arc produced with silver electrode. Nevertheless, the measured conductance, hence the total ionization, is almost the same for the two arcs. Our conclusion must be that in our arc the current is chiefly carried by ionized silver vapour. Indeed, silver has a much lower ionization energy and is therefore easier to ionize than the other components of the arc vapour. Other estimations show that the silver atom concentration is higher than the total electron concentration, which means that the silver can deliver the necessary electrons without the degree of ionization of the vapour being unduly high. In the following estimation we shall neglect the other ionizable atoms and molecules; we suppose the number of silver ions (N_i per cm^3) to be equal to the number of electrons (N_e per cm^3). For the silver vapour Saha's equation then reads:
$N_e^2/N_a = 4.83 \times 10^{15} \times T^{3/2}(Z_i/Z_a) \exp(-\varepsilon_i/kT)$. The concentration N_e of the electrons in the central part of the arc is calculated from $i = Oe\mu_e N_e E$, where i = current = 4.5 amps, O = effective cross-sectional area of the arc $\approx$ 0.05 cm^2 (from fig. 3 an area of 0.05 — 0.08 cm^2 can be derived; we chose the lower value because the diameter of the arc in the figure may be somewhat too large owing to the instability of the arc during the exposure), $e = 1.6 \times 10^{-19}$ coulombs, μ_e = the mobility of the electrons in the arc = $3\frac{1}{2}$ or 4×10^4 cm/sec per volts/cm at 5700°K[11]), and E = axial electric field strength = 30 volts/cm; thus N_e is found to be 5×10^{14} electrons per cm^3. The temperature T in the central part of the arc is somewhat higher than the "mean" temperature; taking this into account we found 5700°K. For silver the ratio of the partition functions (state sums) Z_i and Z_a of ion and atom is $\frac{1}{2}$. The ionization energy ε_i corresponds with 7.57 electron-volts. Substituting all these values in the Saha formula we find for the concentration of the silver atoms N_a the value of 1.2×10^{15} and hence for the total silver concentration $N_a + N_i = (1.2 + 0.5)\ 10^{15} = 1.7 \times 10^{15}$ particles per cm^3.

Probably the first estimate is too high, because silver atoms in the outer region of the arc are caught by chemical binding and conglomeration; furthermore there will be deviations caused by the upper electrode and by the transport of silver ions. Possibly the second estimate is too low, which may be due to the use of a too high value for T (as a rule the silver arc gave somewhat lower values: cf. section 7) and O (as a result of instability of the arc); both factors have considerable influence on $N_a + N_i$. In the following we will use a mean value: $N_a = 1.5 \times 10^{15}$ atoms per cm^3.

Remark: To an electron concentration $N_e = 0.6 \times 10^{15}$ at $T = 5700°K$ there corresponds an electron gas pressure $p_e = 0.0005$ atm.; according to the literature this is a plausible value.

Boltzmann's formula for the degree of excitation of the silver vapour is $N'/N_a = (g'/Z_a) \exp(-\varepsilon'/kT)$. We take, for instance, the spectral line 3982 Å; N', g' and ε' are then, respectively, the population, the statistical weight and the energy of the upper level 8S. Substitution of the values for N_a ($= 1.5 \times 10^{15}$), Z_a ($= 2$), ε' (corresponding to 6.87 electron-volts) and T ($= 5700°K$) in the equation leads to $N' = 6 \times 10^8 g'$. This is the estimated number of silver atoms per cm³ on the level 8S in the central part of the arc.

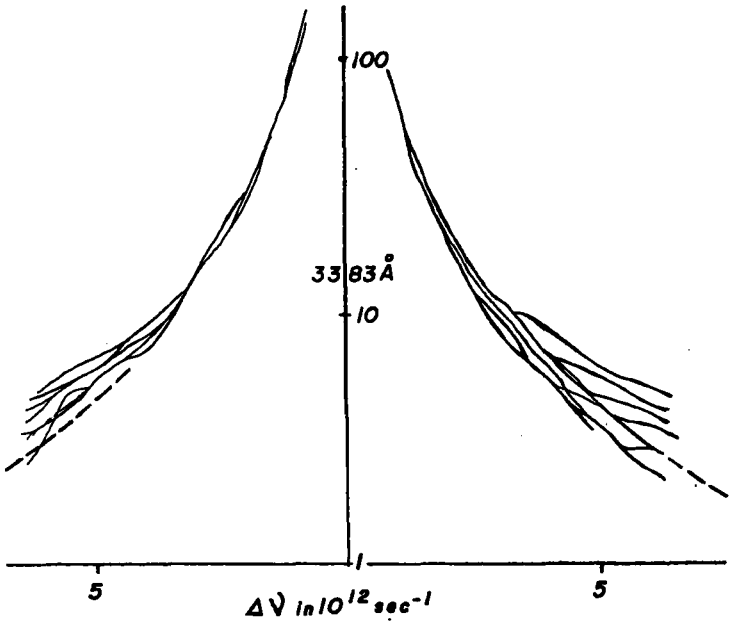

Fig. 9. Logarithmic intensity profile of the silver resonance line 3383 Å (superposition of 8 measurements). The line is very broad in our arc spectra ($\Delta\nu = 10^{13}$ sec^{-1} corresponds with $\Delta\lambda = 38$ Å). The wings have been measured; the central part was disturbed by self-absorption.

For the line 3982 Å the absolute measurement of the intensity gave a radiance (mean of 20 exposures) of $I = 850$ erg sec^{-1} cm^{-2} sterad^{-1}. This relates to the radiation observed in looking along a horizontal line at the centre of a vertical arc. For the production of this radiance the effective diameter of the arc was about 0.2 cm (according to fig. 3 it is 0.23 cm, but we suspected the image to have been broadened as a result of the instability of the arc). For the line 3982 Å the total emission from the central part of the arc was, according to these values, $J = 4\pi \times 850/0.2 = 5 \times 10^4$ ergs sec^{-1} cm^{-3}. If we substitute $J = 5 \times 10^4$, $N' = 6 \times 10^8 g'$ and $\lambda = 4 \times 10^{-5}$ in $J = AN'hc/\lambda$ we find $g'A \approx 1.7 \times 10^7$ sec^{-1}. Thus the relative

values given in column 6 of table I should be multiplied by $1\frac{1}{2}$ or 2×10^7 to produce the actual magnitude of the absolute values.

The resonance lines, 3281 Å and 3383 Å, were not mentioned in the foregoing. It proved not possible correctly to compare their intensities with those of the other lines. At low concentrations of the silver vapour, when the other lines were scarcely measurable, the resonance lines already showed strong absorption. In our ordinary exposures the resonance lines were very wide, with a narrow minimum in the centre owing to self-reversal. Fig. 9 shows the intensity slope in the wings of 3383 Å.

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