

MEASUREMENT OF "OPTICAL" TRANSITION PROBABILITIES OF Cd *)

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Synopsis

Of 31 level combinations in the cadmium atom the probability of spontaneous transition was found with the aid of the spectrum of an arc discharge between carbon electrodes in air with Cd vapour. For that purpose the intensities of the Cd lines were measured on the one side, while on the other side the populations of the upper levels of those lines were calculated from the simultaneously measured arc temperature. The temperature was derived from intensity ratios in the CN bands also occurring in the arc spectrum. The measurements are only relative; since, however, of one line the absolute value of the transition probability was known by other methods the relative results could be converted into absolute values. The results are summarized in table I. Checking measurements showed the absence of disturbing self-absorption etc., and confirmed the validity of Boltzmann's formula for the level populations in the used d.c. and a.c. arcs.

1. *Principle.* When a free atom or molecule of a gas or vapour is in an excited state (with energy ϵ_n), there is always a certain probability (A_{nm} sec⁻¹) that it changes spontaneously into a lower state (energy ϵ_m). In such a transition a photon (with energy $\epsilon_n - \epsilon_m = hc/\lambda_{nm}$) is emitted. The emission per cm³ and per sec is therefore $A_{nm}N_n$ photons, representing $A_{nm}N_nhc/\lambda_{nm}$ erg, in which N_n = number of the considered excited atoms per cm³. The transition probability A is supposed to be an atomic constant ³⁾ just as the wavelength λ of the spectral line.

From the above it appears that the A value belonging to a spectral line can be determined experimentally by measuring the emission intensity of the spectral line and simultaneous measuring of the upper level population N_n , provided the stimulated emission and selfabsorption are negligible. To that end use has often been made of arc discharges between carbon electrodes in air ⁶⁾. The atoms to be investigated, mostly metal atoms, are introduced into the hot arc column by evaporation from an electrode filled with oxide or salt; most compounds dissociate fairly completely at the high temperature in the arc. The excitation of the atoms and molecules in the arc is predominantly thermic, i.e. it is caused by the high temperature of the arc gas ⁴⁾ ⁵⁾ ²⁾. Boltzmann's formula for the level populations, exactly valid in case of

*) abridged contents of thesis ¹⁾.

thermodynamical equilibrium, may therefore be applied to the arc. Thus $N_n = N_{\text{tot}} (g_n/Z) \exp(-\varepsilon_n/kT)$, in which N_{tot} = total number of atoms of the considered element per cm^3 , g_n = statistical weight of the state with energy ε_n , and $Z = \sum_a g_a \exp(-\varepsilon_a/kT)$. With the formula we can calculate the required level population N_n when the vapour concentration N_{tot} and the absolute temperature T in the arc column are known.

Unfortunately it is virtually impossible to calculate with sufficient accuracy the vapour concentration in the arc column from the rate of evaporation of the electrode-filling: the problem of the diffusion and convection becomes a very difficult one because of the great differences in temperature and the possible transport of ionized vapour through the electric field. In this investigation we have therefore confined ourselves to relative measurements (see section 7, however). The ratio of the A values of 2 lines of one substance can be found from their intensity ratios $I_{n'm'}/I_{nm}$ and the arc temperature T ; so the vapour concentration need not be known. For it appears from the above that

$$\frac{I_{n'm'}}{I_{nm}} \frac{\lambda_{n'm'}}{\lambda_{nm}} = \frac{A_{n'm'}}{A_{nm}} \frac{g_{n'}}{g_n} \exp\left(-\frac{\varepsilon_{n'} - \varepsilon_n}{kT}\right),$$

in which $A_{n'm'}/A_{nm}$ is the only unknown when $I_{n'm'}/I_{nm}$ and T are measured. In this way all measurable lines of the element considered can be mutually related.

2. Measuring method. In order to measure the intensity ratio of the spectral lines we photographed the arc spectrum on plates on which also spectra of a calibrated tungsten striplamp were taken. The densities in both kinds of spectra were measured with a recording microphotometer. The spectral lines were traversed in the dispersion direction; the density profiles thus obtained were converted into intensity profiles by means of the striplamp data (see e.g. fig. 2). The area beneath the intensity profile minus the (continuous or non-continuous) "background" was taken as "intensity" of a spectral line. In converting, the striplamp data ($\text{erg sec}^{-1} \text{cm}^{-2} \text{sterad}^{-1} \text{\AA}^{-1}$) were properly divided by the local dispersion, for greater dispersion weakens the continuous striplamp spectra but not the spectral lines. Corrections for solid angles and such were not necessary, since we aimed at relative intensity measurement only. With some lines disturbances were found, which necessitated special techniques; this is discussed in section 5 and 6.

The arc temperature was derived from the intensity ratios in the CN bands that were always present in the arc spectrum. The method has been described and discussed in detail elsewhere ^{5) 6) 7) 8)}. The photographic density profile of the bands (with non-resolved rotational structure) was measured in the dispersion direction and recorded and it was converted into an intensity profile. In our case the areas beneath the intensity profile served as a temper-

ature criterion. We used the ratio of the intensity areas of the 1st, 2nd and 3rd band of the sequence $\Delta v = 0$ (3883 Å etc.) and in some cases $\Delta v = -1$ (4216 Å etc.). For the used calibration curves and further particulars we refer to the thesis ¹⁾.

The intensity ratio of spectral lines and the corresponding arc temperature, needed together for a determination of transition probabilities, were, as a rule, derived from one and the same exposure, in other words, they belonged to one and the same situation in the arc. This was desirable as the arc temperature shows slow fluctuations while the exposure times were often very short (minimum 1 sec). The accidental error was restricted also by our repeated photographing and working out of the spectra; the numbers are given in table I. Systematic errors were looked for by examining whether the temperature and other particulars of the arc had no actual influence on our results concerning the relative A values: see section 4.

3. *Apparatus.* A vertical arc discharge between vertical carbon electrodes in air at atmospheric pressure served as excitation medium. Usually a direct current of 4 to 6 amp was employed, while the lower electrode was anode. For checking purposes also measurements were made with 50 c/s alternating current arcs, stroboscopically (in that case in the lightpath there was a rotating disc with slit, mounted on the axis of a synchronous motor). The upper carbon electrode of the d.c. arc was homogeneous with a diameter of 9 mm; the hollow lower electrode as a rule had an outer diameter of 11 mm and an inner diameter of 9 mm. Of the a.c. arc both carbon rods were hollow. The hollow electrodes were always filled with a mixture containing a little CdO (mostly 1%) and in most cases much ZnO. On account of the fact that these metals have high ionization energies the arc temperature was high (up to about 6500°K); when necessary the temperature was lowered by the adding of NaCl (maximal 5%, in which case T decreased to about 4500°). When measuring with a.c. arcs we employed also the phase-dependency of the temperature. Some of the Cd lines were disturbed by Zn lines; for this reason we made supplementary exposures with AgCl instead of with ZnO. The addition of the Zn or Ag compound was necessary because without such filling matter the Cd lines (with our large inner diameter of the filled electrode) or the CN bands (in case of smaller inner diameter) became too strong. With the above mentioned currents, electrode dimensions, filling matter and mixing ratios the following appropriate conditions could be met:

- a. The arc should burn steadily.
- b. The electrode filling should evaporate quietly, and not slower than the surrounding carbon wall.
- c. The lines to be measured should be sufficiently intense compared with the background in the spectrum.
- d. The lines to be measured should not be so intense as to make the self-

absorption (which is proportional to the initial emission intensity of the line) disturbing.

e. The CN bands should appear on the photographic plate simultaneously with the Cd lines in measurable density (in case of suitable choice of plate and exposure time).

It was not possible to get all investigated Cd lines simultaneously self-absorption-free on the plate in measurable density. They were therefore measured group by group, while the several groups each time had a few lines in common to get the interconnection.

In the calibration department of the laboratory the tungsten striplamp with quartz bulb had been compared at a wavelength of 6500 Å with a black body at the melting point of gold (the radiation of the striplamp was decreased to a well-known extent). In this way the spectral radiance for 6500 Å was found as a function of the lamp current. With the aid of Planck's formula and the emissivity of tungsten, after correction for loss of light due to reflection by the quartz, the temperature of the tungsten band as function of the lamp current had been calculated from the radiance. Starting from the calibration graph thus obtained, we were able to calculate with each desired wavelength the spectral radiance as function of the lamp current. To that end again Planck's formula and the emissivity were used, and a correction for losses due to the quartz. For numerical data we refer to the literature⁹⁾¹⁰⁾; see further the remarks in section 8.

The arc and the tungsten strip respectively were imaged $2\times$ enlarged on the slit of a Littrow type quartz spectrograph (Hilger "Large") by means of a quartz-fluorite achromatic lens. With the arc exposures the slit width was mostly 50 to 70 microns, that is about $2\times$ the critical value. In the ultra-violet where the striplamp emission is relatively weak, the striplamp spectra were taken with a much wider slit than the arc spectra; comparative measurements proved that the errors introduced by this difference were negligible.

4. *Checking measurements.* For most of the checking measurements we may refer to the previous publication²⁾.

The absence of disturbing selfabsorption was proved by the fact that the measured multiplet intensity ratios showed no systematic relation to the Cd concentration in the arc as long as the concentration was not chosen too high. A simple consideration further learns that the error due to stimulated emission is smaller than that due to self-absorption.

The absence of disturbing ionization of the Cd vapour, already expected because of the high ionization-energy of Cd, was confirmed by "cross spectrograms", which showed that the measured Cd radiation came mainly from the central part of the arc, just as the CN radiation does.

The absence of disturbing influence of the electric field between the electrodes, already anticipated on the ground of the relatively low values of

the field strength (fig. 1), was confirmed by the agreement of the A values measured with d.c. and a.c. arcs at different field strength.

A general verification of the correctness of the procedure was obtained by measuring the A ratio of Cd lines with different upper level energy under diverse circumstances in the arc. Table II and III in the previous publication show that with highly different arc temperatures the same A values were found, and with a.c. arcs the same as with d.c. arcs ²⁾.

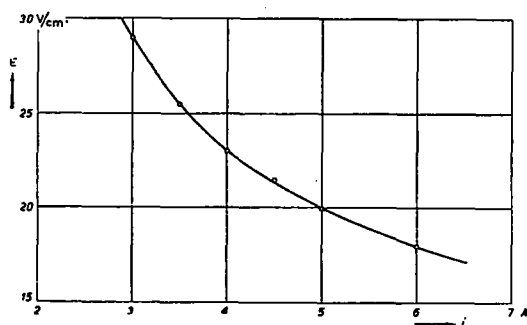


Fig. 1. The axial electric field strength in the d.c. arc, plotted against the current. Lower carbon electrode (anode) filled with 1% CdO mixed in 99% ZnO.

5. *Measurements in the visible spectrum and in the near ultraviolet.* Next follow experimental details concerning the measurements of the individual Cd lines. For details regarding the CN bands also measured, and the necessary striplamp spectra we refer to the thesis ¹⁾. The obtained gA values of the Cd lines are summarized in table I following below.

The gA ratio of the lines 5085.8 and 3610.5 Å, that is the strongest line of the 1st triplet and that of the 1st compound triplet, was measured under various circumstances in the arc; this formed the main part of the general verification of the procedure mentioned in section 4. Use was made of a 5 amp d.c. arc and the phases 30°, 45° and 90° (= temp.max.) of a 6 amp a.c. arc, both with 1% CdO and different Na contents in the electrode filling. The exposure time for the d.c. arc ranged from 1 to 10 sec, dependent on arc temperature. With the stroboscopical a.c. arc exposures this time was naturally longer, namely 30 sec to 2 minutes; in the case with the least high temperature (5200°K at phase 30° and 5% NaCl) in addition more sensitive plates were used. The obtained temperatures, and the intensities and gA ratio of the lines are found in table II and III of the previous publication ²⁾.

The lines 3252.5 and 2980.6 Å, that is the strongest line of the 2nd triplet and that of the 2nd compound triplet, were measured in comparison with the above mentioned (stronger) line 3610.5 Å. For this purpose use was made of a 4 amp. d.c. arc with 1% CdO + 1% NaCl in the ZnO filling, and in addition the phase 45° of a 4 amp a.c. arc with 1% CdO + 5% NaCl. The exposure times ranged from 15 sec to 7 minutes respectively, while in front of the

upper half of the spectrograph slit a platinum-on-quartz weakener (transmission about 0.1) had been placed to moderate 3610.5 Å. For the temperatures etc. we may again refer to table II and III of the previous publication²⁾. So by means of these and the first mentioned measurements the first four multiplets were interconnected.

Partly from the same spectrograms the gA ratios within each of the four multiplets were measured. With the first of the four, the triplet $6^3S \rightarrow 5^3P$ (5085.8 Å etc.), use was made of the 5 amp d.c. arc for the comparison of the components. The results were obtained from 9 exposures with electrode filling 1% CdO in ZnO and 18 exposures with 1% CdO in AgCl. The arc temperature was in the mean 5500° and 5200°K respectively. The use of AgCl was necessary since with ZnO filling the Cd line 4678.2 Å was not measurable because of the Zn line 4680.1 Å. There were no other disturbing lines or bands and the correction for continuous background was relatively

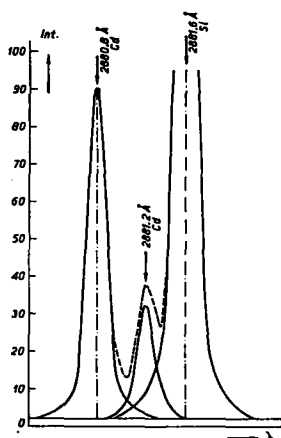


Fig. 2. Intensity profile of the Cd lines $6^3D_2 \rightarrow 5^3P_1$ and $6^3D_1 \rightarrow 5^3P_1$ and the disturbing Si line. Broken line = before the analysis.

small; the intensity of the background was found from other spectrograms which were stronger by a known factor. The exposure time for the Cd lines was 1 sec with ZnO and 2 sec with AgCl.

The ratio of the components of the 1st compound triplet, $5^3D \rightarrow 5^3P$ (3614.4 Å etc.), was derived from 9 plates with together 68 d.c. arc spectrograms suitable for this purpose. By varying the electrode filling and amperage temperatures of 4400° to 6100°K were obtained. Accordingly the exposure time varied from 1 to 10 sec. Correction was needed only for weak continuous background, and this was done in the way described above.

For the measurement of the components of the 2nd triplet, $7^3S \rightarrow 5^3P$ (3252.5 Å etc.), which is much weaker than the 1st triplet, arc temperatures of 5000 to 5500°K appeared to be the most suitable¹⁾. These were obtained

in a 4 amp d.c. arc with electrode filling 1% CdO + 1% NaCl in ZnO and also with phase 45° in a 4 amp a.c. arc with filling 1% CdO + 5% NaCl in ZnO. The triplet was measured in 10 d.c. arc spectrograms with exposure time of 15 sec, and in 11 a.c. arc spectrograms with 7 minutes (which is very long). No disturbing lines or bands occurred.

The ratio of the components of the 2nd compound triplet, $6^3D \rightarrow 5^3P$ (2981.9 Å etc.), was measured in 17 d.c. and 15 a.c. arc spectrograms of the same kind as with the 2nd triplet. The Cd line 2981.3 Å appeared to be disturbed by the Fe line 2981.4 Å. As we did not dispose of iron-free carbon electrodes at the time, we eliminated the disturbance by comparison with a neighbouring Fe line in eight Cd-free spectrograms ¹⁾. The Cd lines 2880.8 and 2881.2 Å were disturbed by the stronger Si line 2881.6 Å. Analysis of these three lines on basis of symmetry of each line separately appeared to be well possible: see fig. 2.

Besides the many lines out of the triplet system only 2 lines out of the singlet system of Cd could be measured. The line $5^1D_2 \rightarrow 5^1P_1$ (6438.5 Å) was compared with $5^3D_3 \rightarrow 5^3P_2$ (3610.5 Å). To that end served 11 spectrograms of a 4 amp d.c. arc with electrode filling 1% CdO + 2% NaCl in ZnO. The arc temperature, 5300°K, does not play an important part, since the upper levels of the lines differ only 0.04 eV. The exposure time was 10 sec on specially sensitive plates; in this case the line 3610.5 Å was measured via the platinum weakener.

The weak singlet line $6^1D_2 \rightarrow 5^1P_1$ (4662.4 Å) was compared with its series partner $5^1D_2 \rightarrow 5^1P_1$ (6438.5 Å) in 7 d.c. arc spectrograms. Of these, 4 were made with arc current 5 amp and electrode filling 1% CdO in ZnO, and 3 with 4 amp and filling 1% CdO + 3% NaCl in ZnO. The arc temperature, 5850° and 5275°K respectively, was important in this case, for the upper levels of the lines differ by 0.73 eV. The exposure time was 25 sec again on specially sensitive (hence coarse grained) plates: 6438.5 Å was now measured via the weakener. The gA ratio amounted according to the two groups of spectrograms to 6.3 : 100 and 5.9 : 100 respectively; the agreement is satisfactory the circumstances considering.

The lines with their gA values so far mentioned have nearly all been stated in table IV in the previous publication ²⁾. Afterwards some corrections have been applied: see section 8. The corrected gA values are found in the table I following below.

6. *Measurements in the far ultraviolet.* The multiplets now to be discussed, the higher numbers of the series, were harder to measure than the preceding ones not only because of the shorter wavelength but also because of the smaller intensity. This made special precautions necessary.

a. At first the false light in the spectrograph was annoying. It could be restricted sufficiently, however, by means of three well-known precautions:

putting a horizontal dark strip across the spectrograph lens, diminishing of the height of the spectrograph slit, and screening off all non-used parts of the photographic plate.

b. In this wavelength region the arc spectrum showed many Fe lines. For this reason, besides the spectra with Cd analogous spectra without Cd were photographed; the nett Cd intensities were found by comparison on logarithmic scale and next subtracting of the intensity profiles, as has been described by Kersten¹¹⁾ and others: see fig. 3.

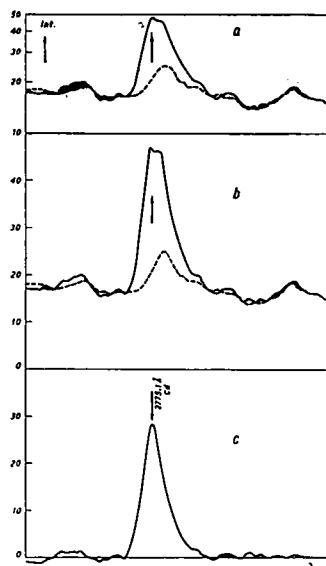


Fig. 3. Intensity profile of the Cd line $8^3S_1 \rightarrow 5^3P_1$ and adjacent "continuum".

a. Measured course of the intensity in a spectrum with Cd (full drawn curve) and in a corresponding spectrum without Cd (broken line). The intensity has been plotted logarithmically against the wavelength, and the curves have been shifted to coincidence outside the Cd line.

b. The same, plotted linearly.

c. Difference between the two curves in *b*, indicating the nett intensity profile of the Cd line.

c. The Cd lines were relatively weak. Their intensities were therefore raised by using a d.c. arc with current 6 to 7 amp and electrode filling 4% CdO in ZnO; the arc temperature then amounted to about 6100°K (or somewhat higher: see the note at foot of table I).

d. The striplamp produces little energy in this wavelength region. It appeared to be necessary, with arc records of 30 sec exposure time and 50 microns slit width, to take the striplamp spectra with 60 sec and slit 3 mm. The systematic errors introduced in this way were negligible.

On account of their greater labouriousness the measurements were less

often repeated than those stated in section 5. This makes the accidental error somewhat greater.

With the above mentioned precautions the following lines or combinations were measured: the two strongest components (2868.3 and 2775.1 Å) of the 3rd triplet, two free components (2763.9 and 2639.5 Å) and two non-divisible

TABLE I

Transition	λ	ϵ	S	g	gA_{rel}	A_{abs} $= 10^5 \times$	Line or multiplet		
$5^1P_1 \rightarrow 5^1S_0$	3261.1	3.78	31	3	0.033	0.0048	Res. int. line		
$5^1D_2 \rightarrow 5^1P_1$	6438.5	7.31	11	5	31.9	2.7 ₆	Singlet line		
$6^1D_2 \rightarrow 5^1P_1$	4662.4	8.04	7	5	1.8	0.16	Singlet line		
$6^3S_1 \rightarrow 5^3P_2$	5085.8	6.35	27	3	17.0	2.4 ₆	1st triplet		
$6^3S_1 \rightarrow 5^3P_1$	4799.9	6.35	27	3	13.8	2.0			
$6^3S_1 \rightarrow 5^3P_0$	4678.2	6.35	18	3	4.0	0.57			
$5^3D_1 \rightarrow 5^3P_2$	3614.4	7.35	10	3	1.5	0.22	1st compound triplet		
$5^3D_2 \rightarrow 5^3P_2$	3612.9	7.35	47	5	16.4	1.4			
$5^3D_3 \rightarrow 5^3P_2$	3610.5	7.34	44	7	100	6.2			
$5^3D_1 \rightarrow 5^3P_1$	3467.7	7.35	56	3	17.2	2.5	2nd triplet		
$5^3D_2 \rightarrow 5^3P_1$	3466.2	7.35	25	5	52	4.5			
$5^3D_1 \rightarrow 5^3P_0$	3403.6	7.35	56	3	23.3	3.4			
$7^3S_1 \rightarrow 5^3P_2$	3252.5	7.72	21	3	6.0	0.87	2nd triplet		
$7^3S_1 \rightarrow 5^3P_1$	3133.2	7.72	21	3	3.8	0.55			
$7^3S_1 \rightarrow 5^3P_0$	3080.8	7.72	18	3	0.9	0.13			
$6^3D_1 \rightarrow 5^3P_2$	2981.9	8.06	6	3	0.5 ₆	0.08	2nd compound triplet		
$6^3D_2 \rightarrow 5^3P_2$	2981.3	8.06	15	5	6.4	0.56			
$6^3D_3 \rightarrow 5^3P_2$	2980.6	8.06	17	7	36.5	2.2 ₆			
$6^3D_1 \rightarrow 5^3P_1$	2881.2	8.06	17	3	6.0	0.86	3rd triplet		
$6^3D_2 \rightarrow 5^3P_1$	2880.8	8.06	14	5	18.5	1.6			
$6^3D_1 \rightarrow 5^3P_0$	2836.9	8.06	17	3	8.0	1.1 ₆			
$8^3S_1 \rightarrow 5^3P_2$	2868.3	8.22	8	3	2.0	0.29	3rd triplet		
$8^3S_1 \rightarrow 5^3P_1$	2775.1	8.22	8	3	1.3	0.18			
$8^3S_1 \rightarrow 5^3P_0$	2733.9	8.22	3	3	0.3 ₆	0.05			
$7^3D_1 \rightarrow 5^3P_2$	2764.1	8.40	8	3, 5	2.7 (2.6)	0.75 (0.72)	3rd compound triplet		
$7^3D_2 \rightarrow 5^3P_2$									
$7^3D_3 \rightarrow 5^3P_2$	2763.9	8.40	8	7	12.1 (11.6)				
$7^3D_1 \rightarrow 5^3P_1$	2677.6	8.40	8	3, 5	8.7 (8.4)	0.38 (0.36)	4th compound triplet		
$7^3D_2 \rightarrow 5^3P_1$									
$7^3D_1 \rightarrow 5^3P_0$	2639.5	8.40	8	3	2.6 (2.5)				
$8^3D_1 \rightarrow 5^3P_2$	2660.4	8.57	8	3, 5, 7	4.3 (4.1)		5th compound triplet		
$8^3D_2 \rightarrow 5^3P_2$									
$8^3D_3 \rightarrow 5^3P_2$	2580.3	8.57	6	3, 5	3.2? (3.0)				
$8^3D_1 \rightarrow 5^3P_1$									
$8^3D_2 \rightarrow 5^3P_1$	2544.7	8.57	—	3	—				
$8^3D_1 \rightarrow 5^3P_0$									
$9^3D_1 \rightarrow 5^3P_2$	2601.5	8.67	5	3, 5, 7	2.1 (1.9)				
$9^3D_2 \rightarrow 5^3P_2$									
$9^3D_3 \rightarrow 5^3P_2$									
$5^3F_2 \rightarrow 5^3P_1$	2862.3	8.09	7	5	0.3 (0.3)	0.02 ₆	Combin. line		

λ = wavelength [Å]; ϵ = energy of upper level [eV]; S = number of exposures and measurements; g = statistical weight of upper level; A_{rel} and A_{abs} = relative and absolute value of the transition probability [sec⁻¹]. For the values of gA_{abs} the reader is referred to fig. 4.

The values in parentheses have been calculated applying Somers' correction to the 4216 Å CN bands, which leads to somewhat higher temperatures than we originally employed.

pairs (2764.1 and 2677.6 Å) of the 3rd compound triplet, a free component and a double and a triple line (2544.7, 2580.3 and 2660.4 Å respectively) of the 4th compound triplet, only a triple line (2601.5 Å) of the 5th compound triplet as the other components were too weak, and finally a combination line $5^3F_2 \rightarrow 5^3P_1$ (2862.3 Å). All these lines were measured in relation to the line $6^3D_1 \rightarrow 5^3P_0$ (2836.9 Å) mentioned in section 5, as this line appeared well measurable in the spectrograms and was not disturbed by other lines. Thus all lines measured so far were brought in relation one to another; table I shows the relative gA values *).

7. *The resonance intercombination line.* This line, $5^3P_1 \rightarrow 5^1S_0$ (3261.1 Å), is important because its absolute A value is fairly well known. By including the line in our relative measurements we obtained the possibility to reduce all our relative gA values to absolute ones. For that reason the measurement of this line was given extra attention.

We first measured with a d.c. arc, after that with an a.c. arc in different phases: see table II. The slit width was 50 microns for the arc spectra and $\frac{1}{2}$ or 1 mm for the striplamp spectra. The arc temperature T is very important in this case because of the great difference in energy of the upper levels of the lines; T was measured with the aid of the CN bands 3883 Å etc. In table II the relative gA values 13.8 and 23.3 respectively for the lines 3403.6 and 4799.9 Å have been derived from table I; the results 0.031 etc. and 0.035 etc. for the resonance intercombination line 3261.1 Å are thus directly comparable and lead to the mean value 0.033 in our relative scale.

TABLE II

D.c. arc		Electrode filling			Exposure time	Number of exposures	Measured ratio	
current		ZnO	CdO	NaCl			gA_{3261}	gA_{3403}
4 amp		98%	1%	1%	1 sec	5	0.031	23.3
4		96	1	3	1	6	0.034	23.3
A.c. arc							$gA_{3261} : gA_{4799}$	
current	phase							
6 amp	90°	99%	1%	0%	15 sec	4	0.035	13.8
6	90	96	1	3	25	5	0.033	13.8
4	45	96	1	3	50	6	0.036	13.8
4	30	99	1	0	20	5	0.029	13.8

With the aid of the magnetic depolarization of resonance-fluorescence Ellett determined the natural mean life τ of the atom in the upper level 5^3P_1 of the resonance intercombination line and found 2.3×10^{-6} sec¹²⁾. Kuhn found 2.5×10^{-6} by means of anomalous magnetorotation¹³⁾. With

*) The gA value of 2580.3 Å in table I may be somewhat too large because of a disturbing line which did not belong to the background but was noticed as it caused a slight deformation of the profile of the 2580.3 line.

their atomic beam method König and Ellett, and Soleillet on the other side arrived at 2.5×10^{-6} ¹⁴) and about 2×10^{-6} ¹⁵) respectively. King and Stockbarger measured the radiation absorption in Cd vapour at this wavelength, which led to $\tau = 2.1 \times 10^{-6}$ ¹⁶). Matland has recently measured the afterglow time of Cd vapour after abrupt termination of the excitation and found $\tau = 2.05 \pm 0.05$ microsec ¹⁷). The mean of the older measurements is therefore 2.3 ± 0.1 microsec, whereas Matland admits no higher than King's value 2.1. The absolute gA values in table I have been calculated by starting from $\tau = 2.1 \times 10^{-6}$ sec i.e. $gA = 1.43 \times 10^6$ sec⁻¹ for the res. int. line; with 2.3 instead of 2.1 the absolute gA values would become 10% lower than stated in table I.

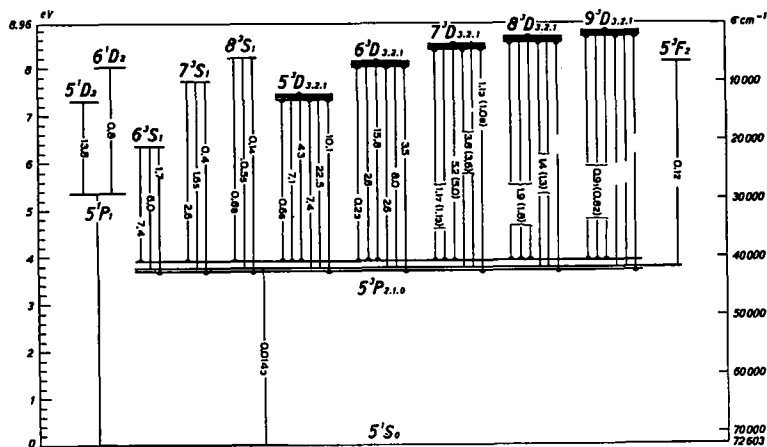


Fig. 4. Energy level scheme with absolute gA values ($\times 10^{-8}$) of the Cd atom. Remarks: In the triple levels the upper component has the highest j value. The absolute gA values are less reliable than their ratios (except for the line 3261 Å). The values in parentheses have been calculated applying Somers' correction: comp. table I.

8. *Remarks in connection with the accuracy of the measuring method.* In order to check the measuring method we should have liked to compare our results with those of others. As has been stated the resonance intercombination line 3261.1 Å has been repeatedly measured elsewhere, while in the literature also for the resonance line 2288.0 Å absolute A values occur. It was therefore obvious to us to measure the A ratio of 3261.1 and 2288.0 and to compare the result with the literature. We did not succeed, however; the resonance line was either too weak with respect to the background or (with greater Cd concentration) too much disturbed by absorption ¹). The very short wavelength and the absorption in Cd vapour near the arc were evidently fatal.

Bates and Damgaard compared some of the relative A values of

triplets and compound triplets calculated by them, with our measuring results¹⁸⁾. The agreement is partly satisfactory.

This latter concerned a comparison with theoretical values. Experimental determination of A values of different Cd triplets by other means than the arc method are not known to us. On account of the high energy of the upper levels of the Cd lines (nearly all above 7.3 eV) one is confined to the arc, the temperature in a flame or furnace not being high enough to obtain sufficient level population.

A comparison with measurements by others thus being impossible we must confine ourselves to an error estimate within our own measurements. With regard to the accidental errors, i.e. the reproducibility, this is fairly simple. The measuring results u concerning one and the same gA ratio scatter round their mean value \bar{u} . When Δ = the mean value of $|u - \bar{u}|$ and δ = the mean error in \bar{u} , so $\delta = \Delta/\sqrt{n}$ (n = number of results), then the following holds:

With most of the lines discussed in section 5,

$$\Delta = 4 \text{ or } 5\% \text{ and } \delta = \text{circa } 1\%$$

With the weak lines 3614.4, 2981.9 and 4662.4,

$$\Delta = 7\% \text{ and } \delta = \text{circa } 3\%$$

With the strongest of the lines discussed in section 6,

$$\Delta = 4\% \text{ and } \delta = 1\frac{1}{2}\%$$

With the weakest of these lines,

$$\Delta = 6 \text{ or } 7\% \text{ and } \delta = 2\frac{1}{2}\%$$

With the res.int.line discussed in section 7, $\Delta = 12\%$ and $\delta = \text{ample } 2\%$

So the general conclusion is that the accidental errors δ in the gA values stated in table I are small.

The systematic errors are more difficult to find but more important. Some will be mentioned; a more extensive discussion is found in the thesis¹⁾. The checkings reported in section 4 are reassuring as to some sources of error, but they do not for instance exclude a systematic error in the calibration of the striplamp, or a systematic error in the measurement of the arc temperature.

As regards the striplamp calibration the measuring results have been brought into line with the use of the radiation constant $c_2 = 1.438$ ⁹⁾ and the emissivity according to de Vries¹⁰⁾, while furthermore attempts have been made to allow for loss of radiation not only by reflection but also by absorption in the quartz bulb and its contamination layer and for other sources of error¹⁹⁾. These (subsequent) corrections are the cause of the difference between the gA values in table I and in earlier tables^{1) 2)}.

When the upper levels of two Cd lines differ much in energy, the intensity ratio of the lines will greatly depend on the arc temperature. In case of level distance $1\frac{1}{2}$ eV and 5000°K the intensity ratio changes 7% per 100° change in temperature. For nearly all measured Cd lines the upper levels are closer together and hence the influence of temperature is smaller. With the res.int. line the difference between line and reference line (see section 7) is 3.57 or

2.57 eV which at 5000° corresponds with 16 and 11% per 100° respectively. The large accidental error $\Delta = 12\%$ with this line is therefore to be ascribed to accidental errors in the measuring of the temperature. Moreover the measured arc temperature will contain systematic errors, quite possibly greater than 100°, among other things because of uncertainty in the employed relative A values of the CN bands⁸⁾. The relative gA value 0.033 of the res.int.line and with it all absolute gA values in table I are consequently far less reliable than the relative gA values of the other lines.

Finally the photographic Eberhard effect should be mentioned as source of error. This effect does not increase the measured intensity of the broad striplamp spectra, but does increase that of the band heads and certainly that of the narrow Cd lines. This error, the errors in the ultraviolet emission of the striplamp, and the uncertainty in the relative A values of the CN bands are, in our opinion, the weak points in the measuring method followed.

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