ON THE EMISSION OF THE FORBIDDEN LINES FROM THE METASTABLE GROUNDSTATES $^1S_0$ AND $^1D_2$ OF THE NEUTRAL OXYGEN ATOM

BY

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§ 1. INTRODUCTORY REMARKS.

As is well known the lines corresponding to transitions from the Metastable *OI* states $^1S_0$ and $^1D_2$ appear in the auroral luminescence. The transition *OI* ($^1D_2 - {}^1S_0$) gives the strong green line, and the transitions *OI* ($^3P_{2,1} - {}^1D_2$) from the $^1D_2$ state to the bottom triplet state $^3P_{2,1,0}$ give the two red auroral lines 6300,30, and 6364,— the enhancement of which causes the red auroral of type A. The lines corresponding to the transitions ($^3P_{2,1} - {}^1S_0$), which no doubt appear in the auroral luminescence, are absorbed in the atmosphere.

The wavelengths of these forbidden lines and the probabilities are given in table I.

Table I.

Transition	Probability		Wavelength	Remarks
$^1D_2-{}^1S_0$	2.0	sec.$^{-1}$	5577,3445	Measured from Aurorae (1)
	»	»	5577,350	» » Nightsky (2)
	»	»	5577,348	From *OI* in Discharge (30)
	»	»	5577,356	From *OI* Term Values (29)
$^3P_1-{}^1S_0$	0,18	«	2972,257	Obs. in Lab. experiments (3,33)
$^3P_2-{}^1S_0$	$0{,}16{,}10^{-3}$	»	2958,348	Calc. from term values (3)
$^3P_0-{}^1S_0$	0	«	2978,337	» » » » (3)
$^3P_2-{}^1D_2$	$7{,}5.10^{-3}$	»	6300,304	Measured from Aurorae (5, 6, 7)
	»	»	6300,23	From *OI* Discharge (3)
	»	»	6300,332	Calc. from term values (3)
$^3P_1-{}^1D_2$	$2{,}5.10^{-3}$	»	6363,85	Measured from Aurorae (8)
	»	»	6363,88	From *OI*. Discharge (3)
	»	»	6363,75	Calc. from term values (3)
$^3P_0-{}^1D_2$	0	»	6391,68	» » » » (3)

If (n) is the average number of atoms existing in the upper state at the time considered, the intensity of the line will be;

$$I = n\,A\,h\nu \qquad (1)$$

where A is the transition probability, (ν) the frequency and (h) Plancks constant. It follows from equation (1) that the two lines 2978 and 6392 for which $A = 0$, do not appear.

For the intensities I_1 and I_2 of two lines corresponding to the same upper state, we have:

$$I_1/I_2 = \frac{A_1\nu_1}{A_2\nu_2} \qquad (2)$$

In the case of the two trans-auroral lines we find:

$$\frac{I\,(^3P_1 - {}^1S_0)}{I\,(^3P_2 - {}^1S_0)} = 1100$$

This means that only the line 2972 is observable.

For the red doublet we find:

$$\frac{I\,({}^3P_1 - {}^1D_2)}{I\,({}^3P_2 - {}^1D_2)} = 0{,}33 \qquad (3)$$

If the transition probabilities from a given upper state are A_1, $A_2\ldots$, the average lifetime (τ) of this state is

$$\tau = \frac{1}{\Sigma A} \qquad (4)$$

This gives for the ${}^1S_0$ state $\tau = 0{,}46$ sec. and for the ${}^1D_2$ state $\tau = 100$ sec. When the excited atom is left undisturbed to itself, the lifetime of the ${}^1D_2$ state should be about 220 times as large as that of the ${}^1S_0$ state.

As shown by Vegard and collaborators and others (9, 10, 11, 8, 12, 13, 14, 15, 16, 17, 18, 19) the intensity of the red doublet relative to that of the green line fluctuates very largely in the auroral luminescence under various circumstances. As a rule the green line appears with dominating intensity in the auroral spectrum, the red doublet, however, is usually very weak so that its intensity may only be a minute percentage of that of the green line. Under certain conditions the red doublet is enormously enhanced. As far as our present observational evidence goes the relative intensity of the red doublet is found to fluctuate between the following limits:

$$1/100^1 < \frac{I_{6300}}{I_{5577}} \overset{=}{<} 6^2 \qquad (5)$$

In order to explain these fluctuations, when seen in relation to the conditions under which they occur, a number of possibilities have been suggested (22, 11, 23) but as yet we cannot claim to have found the true explanation of the many variability effects found for the ratio I_{6300}/I_{5577}.

On the other hand the intensity variations within the auroral spectrum are of the greatest interest and their interpretation will no doubt contribute largely to our knowledge of the physics of the auroral region (Ionosphere).

As a step in this direction we think it is very important to study the excitation of the metastable OI states and the emission of the forbidden lines under such conditions as may be produced in laboratory experiments.

Preparations for such experiments were made at the Physical Institute several years before the war. Some preliminary experiments were made in 1939—40 with the collaboration of Mr. B. C. Landseer-Jones, but as a British citizen he was sent to Germany soon after the occupation of Norway.

The work was continued during the subsequent two years and most of the experimental results dealt with in this paper, had been obtained by the spring of 1942. Some additional experiments which were finished in 1943. will also be included.

§ 2. PREVIOUS WORK RELATING TO THE GREEN AND RED AURORAL LINES.

In 1925 Mc. Lennan and Shrum (27) observed the green auroral line in the luminescence from a discharge through oxygen and through mixtures of oxygen and one of the inert gases Helium, Neon or Argon, and showed that it originated from oxygen.

From observations of the Zeeman effect Mc. Lennan, Mc. Leod and Ruedy (25) were able to show that the green auroral line originated from a forbidden transition (${}^1D_2 - {}^1S_0$) between the metastable groundstates of the neutral oxygen atom. L. A. Sommer (26) reached in a similar way the same conclusion.

The energy levels of the metastable states ${}^1S_0$ and ${}^1D_2$ relative to the bottom states ${}^3P_{2,1,0}$ were determined from investigations by Hopfield (27, 28, 3) and Frerichs (29) of the ultraviolet OI-spectrum. Within the limit of error the wavelength calculated from the known term difference (${}^1D_2 - {}^1S_0$) was equal to that of the green OI-line observed by Mc. Lennan and Shrum. Very accurate measurements of the wavelength of the green OI-line were made by Cario (30) who found the wavelength $\lambda = 5577{,}348 \pm 0{,}005$ Å, which agrees very well with the value 5577,35 obtained by Babcock (2) from the night sky and the value 5577,3445 found by Vegard and Harang (1) from the aurorae.

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[1] Compare paper 11, 20 and 21.

[2] » » (8) p. 20.

From the known term values of the $^1D_2$ and $^3P_{2,1,0}$ states the wavelengths of the components of the triplet corresponding to the transitions $^3P_{2,1,0} - {}^1D_2$ were found to be 6300, 6364, 6392. As already mentioned the intensity of the third component is zero. The two stronger ones correspond to the red auroral lines which in certain cases are so strong that the aurorae appear red. (Red Aurorae of type A.)

The first spectrograms of the red doublet were taken with spectrographs with small dispersion and somewhat wide slit so the components were not separated (31) (10). Both components were measured by Vegard from an auroral spectrogram, obtained during the winter 1931—32 (4). The wavelength of the strongest component was very accurately measured with Fabry-Perot interferometers by Vegard and Harang (5) and by Vegard (7). The mean value derived from these observations was found to be: $\lambda = 6300{,}304 + 0{,}010$ Å (I.U.)

During resent years the wavelength of the second component was measured by Vegard and Tønsberg (8, 32) from auroral spectrograms giving considerable separation of the two components. The mean value of the wavelength was found to be

$$\lambda = 6363{,}8 \text{ Å}.$$

The red OI-doublet was obtained by Hopfield in 1930 (31) on spectrograms taken at the Paschen Institute from heavy discharges through oxygen. The results of wavelength measurements from the spectrogram were published by Paschen (33) who even gives the wavelength 6391 of the third component. The final inspection and measurements undertaken by Hopfield (31) gave the following wavelength values for the two strongest components: 6300,23 Å and 6363,88 Å, but no third component.

It appears from this short summary of previous investigations that the forbidden OI-lines corresponding to the transitions from the metastable ground states $^1S_0$ and $^1D_2$ of the neutral oxygen atom have been reproduced in laboratory experiments. Spectrograms of the green line have been obtained with grating spectrographs of high dispersion and its Zeeman effect analysed. Hopfields spectrograms of the observable two components of the red doublet were obtained with a spectrograph of the somewhat moderate disperssion of 29 Å per mm.

The relative intensity, however, of the components of the red doublet has not been accurately measured from light sources produced in laboratories.

Although these forbidden OI-lines have been obtained from artificial light sources, no thoroughly systematic study has been done regarding the intensity with which these lines appear under various physical conditions.

Results of investigations into the nature and the occurence of the auroral green line 5577 have been published by Mc. Lennan, Mc. Leod and Quarrie (34). In this paper they give certain data regarding the influence of current and pressure on the appearence of the green line, but the paper does not deal with the red triplet.

The object of our investigations has been to undertake a more systematic study of the influence of current, pressure, tube dimensions and concentration of an inert gas on the intensity of both the green line OI ($^1D_2 - {}^1S_0$) and the two components of the triplet OI ($^3P_{2,1,0} - {}^1D_2$) including measurements of the wavelengths and relative intensities of the red components.

§ 3. THE EXPERIMENTAL PROCEDURE.

By the planning of our experimental arrangements, we utilised the experiences gained by the previous workers in this field and already referred to. Above all we have to take into account that an oxygen atom in one of the metastable states ($^1S_0$ or $^1D_2$) will lose its excitation energy when it strikes the surface of any solid body inside the discharge tube. This involves the advantage of using fairly wide tubes and not too low pressure and mixing oxygen with inert gases of excitation potentials higher than that the $^1S_0$ state.

In order to obtain spectra of suitable density with the shortest possible exposure, the tube should be run with a large current.

The vacuum system is illustrated in fig. 1. The oxygen gas is produced in the bulb R_1 by heating $KMnO_4$ after careful evacuation. The O_2-gas may be gradually transfered to the receiver R_2 through the taps C_1 and C_2 and the vapour-trap t_1, cooled with liquid air. By means

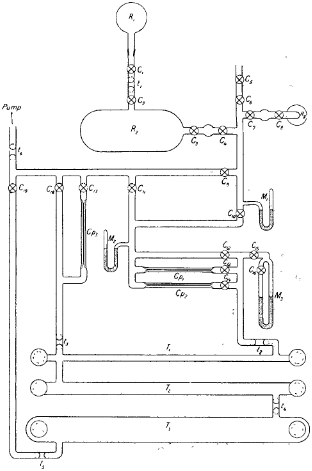

Fig. 1.

of the taps C_3, C_4 small portions of O_2-gas could be introduced into the vacuum system, and in a similar way the inert gas to be used was introduced into the same system from the receiver R_3 through the taps C_7 and C_8. During this operation the taps C_6, C_9 and C_{10} were kept closed. In order to increase the volume of the mixture, the tap C_{10} was opened while C_{11} and C_{12} were closed. The partial pressures of the components of the mixture were measured by the Mercury gauge M_1 or M_2.

By opening one of the taps C_{13} or C_{14} a current of gas could be maintained through one of the capillaries C_{p_1} or C_{p_2} into the discharge tubes T_1, T_2 and T_3. By adjusting the gas-pressure in the reservoir to the pump velocity, the gas pressure in the discharge tubes could be kept constant as desired.

In order to obtain a suitable pressure in the discharge tube without using too much gas, the gas current was slowed down by letting it pass through the somewhat wide capillary C_{p_3}.

Vapours of any kind were prevented from entering the discharge tubes by means of the traps t_2, t_3, t_4, t_5 and t_6, which were cooled with liquid air. The total pressure in the discharge tubes was measured by an oil gauge M_3. When the tubes had been run for some time and allowed to give off vapours and gases occluded in the walls and the electrodes, the gascurrent could be stopped by closing the taps leading to the pump and the gas-container. Continued run-

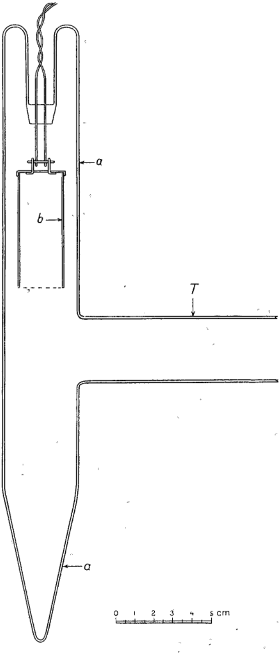

Fig. 2.

ning of the tube did not essentially effect the pressure or the spectral purity of the gas.

The form of the discharge tubes is indicated in fig. 2. The electrodes which consist of nickel cylinders (*b*) open at the lower end, are mounted in two equal side tubes (*a a'*) one at each end of the horizontal part (*T*) giving the positive column to be analysed by end- on exposure. All tubes used had about the same length, viz. 68 cm.

We have worked with two sets of tubes. In a first series of experiments the vacuum system, as indicated in fig. 1, was provided with three discharge tubes with internal diameters: 12, 33 and 51 mm.

In a second series four tubes were put up with the following internal diameters: 7.8 — 15.8 — 32.8 — 62.2 mm. In this way we managed to get all tubes of each set at the same time filled with gas of the same pressure and composition, which is a matter of importance for the study of the influence of the tube diameters on the intensity of the forbidden lines.

The electrical arrangement consisted of a hightension transformer giving a tension of 10.000 Volts and a maximum current of 0,5 Ampères. The primary current was regulated by means of a variable Rheostat provided with an Am.meter and a voltmeter. The discharge current was measured with a galvanometer in the secondary circuit, and the tension on the discharge tube was measured with the same galvanometer connected in series with a high resistence of 1,28 M.Ohm.

The present paper deals with experiments in pure oxygen and in mixtures of Neon and Oxygen. Neon of a guaranteed purity of 99.8 % was obtained from "Norsk Hydro". This purity was found satisfactory for our purpose.

The total pressure was varied between 1,5 and 50 mm. The oxygen concentration of the ($Ne - O_2$) mixtures was varied from 1,5 %—48 %. The discharge current was varied from 25—150 m Amp.

§ 4. REMARKS REGARDING THE SPECTROGRAPHIC WORK.

As already indicated, one of the principal objects of the investigation here dealt with was to study the variations of the intensities of the forbidden *OI* lines, seen in relation to those of the permitted *OI*-lines under various physical conditions e. g. as regards current, pressure, oxygen concentration and tube diameter. For this purpose a large number of spectrograms should be taken and the dispersion should be large enough to give a fairly good separation of the lines. Accordingly most of our spectrograms were taken with a spectrograph combining a high light power with a fairly good dispersion. The instrument had two 60° prisms and two 30°, and the geometrical aperture of both the collimator and the kamera lens was F: 3. In the region 5300—5600 the dispersion varied from 110—140 Å/mm. Spectrograms of suitable photographic density were usually obtained with an exposure of a few minutes.

An intensity scale was as a rule photographed on the same plate. By the determination of the wavelength of a line on these spectrograms we used the interpolation formula:

$$\lambda = \lambda_0 + \frac{a}{s + b} \tag{6}$$

where (λ_0), (a) and (b) are constants to be determined from three known lines λ_1, λ_2, λ_3 situated in the interval considered, and (s) is the distance on the spectrogram from the line to the standard line (λ_2).

In order to obtain more accurate wavelength measurements of the forbidden lines and to obtain spectrograms which gave better conditions for an accurate determination of the relative intensities of the two components of the doublet ($^3P_{2,1} - {}^1D_2$) we took a number of spectrograms with a 1 m grating spectrograph. Its light power being very small, exposures of at least 150 hours had to be used.

In the case of the grating spectrograms the dispersion remains nearly constans. By means of known standard lines we found:

In the interval 6600–6000 a dispersion = 17,12 Å/mm
» » » 6000–5300 » » = 17,05 »

§ 5. ON THE PROCEDURE FOLLOWED BY THE DETERMINATION OF RELATIVE INTENSITIES OF SPECTRAL LINES.

In order to compare intensities of lines of different wavelengths we took with the same spectrograph and on the same plate as the line spectra to be measured, a series of spectrograms with varying exposure from a light source of known spectral energy distribution.

The photographic density was evaluated by means of a Moll registering photometer. The deflection of the registering galvanometer is supposed to be measured from an arbitrary horizontal line on the photogram. Let the deflection corresponding to the ground fog on the plate be (δ_g). A spectral line (λ), for which the intensity per unit area on the plate is (i), is supposed to give a deflection (δ), then according to the law of Schwartzschild:

$$it^p = \varphi_\lambda (\delta - \delta_g)$$

or putting $\delta - \delta_g = u$.

$$it^p = \varphi_\lambda (u) \quad \ldots\ldots\ldots\ldots \quad (7_a)$$

(t) is the time of exposure and (p) Schwartzschild's constant.

The intensity scale consisted of a series of spectra taken with a constant light source with exposure times varying in the proportion 1 : 2 : 4 : 8. This will have the same effect on the photographic density as if the time of exposure had been kept constant and the intensities varied in the proportion $1^p : 2^p : 4^p : 8^p$. Thus the relation between (i) and (u) for a constant time of exposure is found by plotting the curve ($t^p - u$), putting (t^p) as abscisse and (u) as ordinate. For any value (u) of the photographic density there is a corresponding value of t^p, which gives a relative measure of intensity. In this way the curve gives a representation of the function $\varphi_\lambda (u)$.

Plotting the curves corresponding to different wavelength values, we find that the function $\varphi_\lambda (u)$ for different wavelength values only differs by a constant factor, which for a certain spectrograph under given conditions and for photographic plates of the same quality is a function of the wavelength (λ).

The equation (7_a) then takes the form:

$$k_\lambda it^p = \varphi (u) \quad \ldots\ldots\ldots\ldots \quad (7_b)$$

Let the intensity pro unit area of homogeneous light (eg. a spectral line) falling on the slit of the spectrograph be I, then the intensity (i) pro unit area of the image falling on the plate will be ($q_\lambda I$) where (q_λ) is a factor depending on the wavelength in a way which is charachteristic of the spectrograph used. Then from equation (7_b).

$$I = \frac{\varphi (u)}{q_\lambda k_\lambda t^p} = \frac{\varphi (u)}{Q_\lambda t_p} \quad \ldots\ldots\ldots\ldots \quad (8)$$

where

$$q_\lambda k_\lambda = Q_\lambda$$

If we have a series of spectrograms taken on the same plate, with the same spectrograph in the same position relative to the discharge tube, and the time of exposure is observed for each spectrogram, then the relative intensity by which any line is emitted from the light source can be found from equation (8) provided we know the value of (Q_λ) as a function of (λ).

The value of Q_λ is found from spectrograms taken with a standard lamp from Kipp & Zonen, Holland.

When the lamp is placed at a certain distance from the slit, the total intensity falling on unit area of the slit aperture is given by the equation:

$$I_s = A \int_0^\infty E_\lambda d\lambda$$

The values of E_λ for various currents and wavelengths are given in tables following the standard lamp.

At a certain point on the spectrogram correspondig to a certain wavelength λ, the intensity falling on unit area of the plate can be expressed:

$$i = bq_\lambda \frac{dI_s}{d\lambda} \frac{d\lambda}{ds} = bAq_\lambda E_\lambda \frac{d\lambda}{ds} \quad \ldots\ldots \ldots \quad (9)$$

where (b) is the width of the slit aperture. Using equation (7_b)

$$bAq_\lambda E_\lambda \frac{d\lambda}{ds} = \frac{\varphi (u)}{k_\lambda t^p}$$

or

$$q_\lambda k_\lambda = Q_\lambda = \frac{\varphi (u)}{kE_\lambda \frac{d\lambda}{ds}} \quad \ldots\ldots\ldots\ldots \quad (10)$$

where $k = bAt^p$ is a constant independent of λ. From a registram along the continuous spectrum $\varphi (u)$ can be found for any wavelength and, knowing E_λ and the dispersion $\frac{d\lambda}{ds}$, we find the quantity Q_λ as a funtion of λ.

Table 2.

λ	Q_λ
6500	2,95
6400	3,54
6300	3.99
6200	4,43
6100	4,55
6000	4,46
5900	4,04
5800	3,83
5700	3,97
5600	4,64
5500	5,69
5400	6,61
5300	7,59
5200	7,82
5100	7,73
5000	6,45

Relative values for Q_λ for different values of (λ) found for one of our plates are given in table 2.

It often happens that the ground density near a spectral line is considerably greater than the ground fog on the plate as a whole. Let the deflection of the registering instrument close to the line be δ_1, and that of the line itself δ_2 then:

$$u_1 = \delta_1 - \delta_g$$
$$u_2 = \delta_2 - \delta_g$$

Assuming the density corresponding to u_1 is due to light of intensity i_1 superimposed on the light of the spectral line of intensity i_2, we have from equation (7b):

$$i_2 + i_1 = \frac{\varphi(u_2)}{k_\lambda t^p}$$

$$i_1 = \frac{\varphi(u_1)}{k_\lambda t^p}, \text{ and}$$

$$i_2 = \frac{\varphi(u_2) - \varphi(u_1)}{k_\lambda t^p}$$

Applying equation (8):

$$I_2 = \frac{\varphi(u_2) - \varphi(u_1)}{Q_\lambda t^p} \quad \ldots\ldots\ldots (11)$$

In order to make all measurements comparable, all deflections (u) must be reduced to the same sensitivity of the photometer or the same value of $u_{\max} = \delta_\infty - \delta_0$ where (δ_∞) is the deflection corresponding to an intransparent plate and (δ_0) is the deflection we get when no plate is placed in the path of the light beam of the photometer.

The procedure here described should give principally the true relative intensity of the emitted lines when the spectrograms, including those of the intensity scale, are all on the same photographic plate.

Spectrograms and scales taken on different plates will also be approximately comparable, when we use the same kind of photographic plates, exactly the same process of development and when all spectra to be compared are taken with the same spectrograph in the same position relative to the same discharge tube, and the same width of the slit is used the whole time.

If we want to compare the intensities of spectral lines corresponding to discharge tubes of different diameters, the spectra to be compared can be taken on the same plate. The intensities (I) passing the slit are calculated by means of equation (8). The intensities thus found will give approximately the true relative energy emitted pro unit volume ot the positive column of the discharge tube, provided the following conditions are fulfilled:

a) The axis of the collimator coincides with that of the positive column.
b) The distance between the slit and the end of the tube is the same.
c) No essential part of the spectrograph is altered.
d) The space-angle of the collimator (the effective light cone) is completely and evenly filled with radiation.

Conditions (a), (b) and (c) have been fulfilled quite satisfactorely, and the last condition (d) with a fairly good approximation.

§ 6. THE SPECTROGRAMS.

The green and red auroral lines corresponding to the metastable ground states of the oxygen atom were obtained in mixtures of O_2 and Ne as well as in pure oxygen. A spectrogram from pure oxygen at a pressure of 2,4 mm Hg is reproduced on Pl I spectrogram A.

The green auroral line (5577) is seen to appear with considerable intensity, and the red doublet — 6300 and 6364, although weak —

also appears quite distinctly. In addition a number of the ordinary *OI*-lines appear. Among these the line 4368, which is found in the auroral spectrum, is particularly prominent. Some very weak *OII*-lines in the region 4676—4350 were observed.

By lowering the pressure the relative intensity of the forbidden *OI*-lines decreases and at a pressure of 0,5 mm the oxygen bands ($b^4\Sigma - a^4\Pi$) appeared with considerable intensity on the spectrograms.

A vibrational sequence of these bands is situated in the interval 5595—5565 and masks the green auroral line. This makes it difficult to study the appearance of the green line at such low oxygen pressures, at any rate with the prism spectrograph we used.

For each concentration of the O_2 — Ne mixtures, we took with the prism spectrograph one series of spectrogrrams with constant total pressure and varying discharge current, and one with constant current and varying pressure.

For the study of the variation of the line intensity with the diameter we used pure oxygen.

The spectrograms are given on plates I and II and arranged in such a way that the spectrograms of each series form a group, where the spectrograms are put close together.

The series of spectrograms corresponding to constant concentration and pressure and varying current are given on Pl. I Groups B—G. Group H plate I is a series from the tube T_2 and pure oxygen at a pressure of 4,5 mm Hg and varying current. Plate I, group I, K, L, M are series from pure oxygen corresponding to different tube-diameters. The groups A—E, Pl. II represent series of different concentrations, where the spectrograms within each series correspond to constant current and concentration and varying total pressure.

The groups F, G, of Pl. II are spectra taken with tube T_2 of pure oxygen at different pressures, but nearly constant current. Group H, pl. II, corresponds to tube T_3 with pure oxygen, constant current and varying pressure. Pl. III gives reproductions of five spectrograms taken with the 1 m grating spectrograph. In the case of spectrograms (a), (b), (c) and (d) the tube contained pure oxygen at pressures varying between 2,5 and 4 mm and currents varying between 150 and 200 m.A.

The spectrogram (e) corresponds to the discharge in a Ne — O_2 mixture containing 80 % O_2. The green and red auroral lines appear quite distinctly and well separated from other lines.

All spectrograms were taken on Agfa Isopan ISS plates. In order that intensities measured from spectrograms taken on different plates might be as nearly as possible comparable, the photographic plates used in the prism spectrograph were not sensitized.

In the case of the grating spectrograph however, the plates were sensitized with NH_3 in order to reduce the time of exposure. This could be done because in that case we only wanted to make wavelength measurements and to compare intensities of lines on the same spectrogram.

The important data relating to each spectrogram are given in the tables «Explanation of the plates» printed at the end of the paper.

The potential differens (V) between the electrodes varied somewhat with current and pressure, but normally it had a value near 1800—2000 volts. Some times, however, the potential assumed an exceptionally low value without any corresponding change of pressure and current. This reduction of potential was accompanied by a large drop in the light intensity of the tube

It seems at if, for some reason, a change of the discharge mechanism has taken place. Such changes have been observed by one of us (Vegard) (36) when the positive column passes from the continuous into the striated form. As we use alternating current and a fairly high pressure, the striated structure of the positive column can not in the present case be observed directly by the eye, even if it existed.

To illustrate this effect we may refer to the table giving the explanation of pl. II, where the potential (V) for the groups F, G and H corresponding to discharges through pure oxygen are given. Spectrogram No. 10 of group G is very much weaker than the others of the group, and we notice that although pressure and current are increased, the potential has dropped from 2050 to 1100 volts.

A similar case is found for spectrograms

No. 9 of group H. Although pressure and current is nearly the same as for spectrogram No. 8, the potential has dropped from 1900 to 930 volts and the light intensity is enormously reduced.

The time of exposure of spectrum No. 9 is nearly four times as large as that of No. 8 while the photographic density is only a small fraction of that of the other spectrograms of the group. The fact that this change of the discharge mechanism occurs at the end of each series, indicates that it is in some way connected with the presence of traces of impurities gradually produced during the discharge.

It is evident that spectrograms which correspond to different types of discharges are not comparable as regards intensities of spectral lines, and the examination of the tension gives a valuable indication of the comparability of the spectrograms. Comparable spectra must also fulfil the conditions that they correspond to reversible discharge conditions, so that the line intensities are independent of the order of operation. Only when this condition is obtained, is the intensity a single valued function of discharge conditions, such as current, pressure, tube diameter and O_2 — concentration. This means that series of spectrograms showing pronounced hysteresis phenomena are not comparable.

§ 7. DETERMINATION OF WAVELENGTH AND RELATIVE INTENSITY OF THE FORBIDDEN OI-LINES BY MEANS OF THE GRATING-SPECTROGRAMS PL- III.

The spectrograms from pure oxygen Pl. III a, b, c, d were taken with a long slit. A Ne-comparison spectrum was taken with both ends of the slit covered. In the case of the last spectrogram Pl. III e, corresponding to a mixture of O_2 and Ne, no comparison spectrum was needed, because the spectrum from the discharge tube itself showed a number of Ne-lines.

Two other spectrograms were taken for O_2–Ne mixtures, but as the line 6364 was too weak for intensity measurements, these spectrograms were not reproduced on Pl. III. The line 6300, however, appeared quite distinctly, so these spectrograms gave favourable conditions for an accurate determination of this line by using Ne-line 6304,79 as a standard of reference.

In the case of the spectrograms (a, b, c) from pure oxygen, the Ne-comparison spectra showed irregularities, and we used known OI lines for comparison. As the dispersion is nearly constant, the wavelength could be found by measuring the distance (Δs) on the plate to a known line, and the corresponding difference of wavelength ($\Delta \lambda$) was found by multiplying (Δs) by the mean dispersion $\left(\frac{d\lambda}{ds}\right)$ of the interval considered. The dispersion curve could be determined with great accuracy.

The results of the wavelength measurements of the green and red auroral lines are given in table 3.

The lines finally used as standard-lines of reference are given at the bottom of the table.

Table 3.

Pl. III Spectr.	5577,+	6300,+	6363,+
a	0,37	0,29	0,82
b	0,33	0,27	0,85
c	0,33	0,32	0,89
d	0,35	0,29	0,84
e	0,35	0,31	0,87
Not reprod.		0,28	
» »		0,32	
Mean	5577,346	6300,297	6363,854
Standard lines of reference	5554,94	6304,79 Ne 6456,01 4.48 } OI 3,64 6158,19 6,78 } OI 5,99	6300,304

The weaker red component was measured relative to the strongest one, for which the wavelength has been very accurately measured from the auroral luminescence. The mean values found for the forbidden *OI*-lines agree well with those previously found given in table 1.

The wavelength 6363,854 here found for the weakest red component we consider to be the most accurate as yet obtained, because all previous determinations of this line are either based on spectrograms of much smaller dispersion, or derived from term values calculated from the ultraviolet spectrum.

The following values of the wavelengths of the forbidden OI-lines may at present be regarded as the most accurate:

$$^1D_2 - {}^1S_0,\ \lambda = 5577{,}345$$
$$^3P_2 - {}^1D_2,\ \lambda = 6300{,}304$$
$$^3P_1 - {}^1D_2,\ \lambda = 6363{,}854$$

When we know the term values of the normal ground state $^3P_2$, the three lines give us the term values of the states $^3P_1$, $^1D_2$ and $^1S_0$. The term $^3P_0$ must be fixed by means of the ultraviolet spectrum. The term values of the states $^3P_2$ and $^3P_0$ have recently been redetermined by Edlén (37).

When we use Edléns values for these two states the wavelengths of the green and red lines lead to the term values of the other metastable OI-states given in table 4.

Table 4.

Atomic states	Term values		
	Hopfield	The Authors	Edlén
$^3P_2$	109 837,30	109 836,7	109 836,7
$^3P_1$	109 679,17	109 678,24	109 678,2
$^3P_0$	109 610,52	109 610,2	109 610,2
$^1D_2$	93 969,50	93 968,83	93 969,0
$^1S_0$	76 044,50	76 044,12	76 044,3

The term values found by Hopfield and Edlén are also given in table 4 for the sake of comparison.

The relative intensities of the green line and of the two red ones were measured in the way previously described by using the equations (8) and (10).

The results are given in table 5.

Table 5.
Relative Intensities
of the Green and Red Forbidden OI-Lines
From the Grating Spectrograms, Pl. III. Tube T_2.

Spectr:	a	b	d	e	Means
6363,8	0,34	0,32	0,32	0,35	0,33
6300,3	1,00	1,00	1,00	1,00	1,00
5577,3	2,90	1,78	2,24	3,01	(2 5)

The intensity of the line 6300 is taken as equal to 1.

As already stated in the introduction, the intensity of line 6364 relative to that of the line 6300, should be constant and equal to 0,33. The variations shown by the values obtained from the different spectrograms are due to error. The mean experimental value 0,33 agrees remarkably well with theory.

The intensity ratio I_{5577}/I_{6300} will depend largely on the physical conditions, and the fluctuations shown by the relative intensity of the line 5577 are no doubt real.

§ 8. THE VARIATION OF THE INTENSITY OF OI-LINES WITH DISCHARGE CURRENT.

For each spectrogram the intensities of the forbidden OI-lines and a number of the more pronounced permitted OI-lines were measured in the way described in § 5.

The intensity measurements gave the result that the *relative* intensities of both forbidden and permitted lines within the limit of error, at constant pressure, are independent of the discharge current.

It was found that the relation between the intensity I of a certain OI-line and the discharge current (i) can be expressed by the formula:

$$I = K i^n \ldots\ldots\ldots\ldots\ldots \quad (12)$$

This means that log I is a linear function of log i.

The correctnes of this relation is illustrated by the curves in fig. 3 a and fig. 3 b. Fig. 3 b gives the relation betwen log I and log (i) of the permitted OI-line 5555 for a number of different O_2-concentrations of Ne–O_2 mixtures. Lines corresponding to different concentrations run parallel, which means that they give same value of $n = 1{,}66$, but different values of K. in equation (12).

The corresponding curves for the forbidden line 5577 given in fig. 3 a give a value of $n = 1{,}68$, which within the limit of error is identical with that found for the permitted line. Thus for all OI-lines the variation of the intensity as a function of the current in the interval of our observations, is given by the formula (12) where $n = 1{,}67$.

Also in the case of discharge through pure

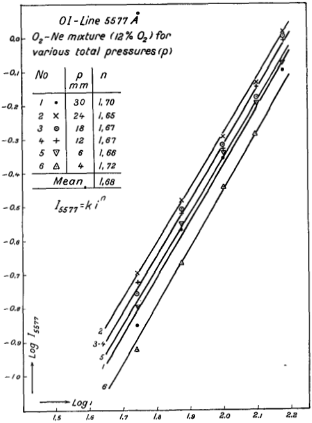

Fig. 3 a.

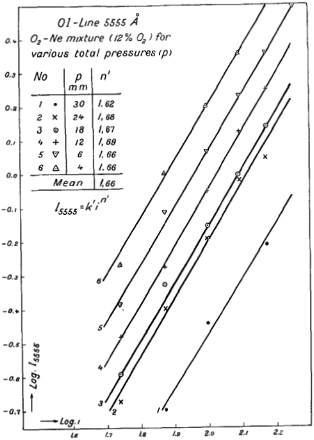

Fig. 3 b.

oxygen, we find that the intensity of a forbidden line relative to that of a permitted one is independent of the current. This is shown in table 6, where the intensity ratio I_{5577}/I_{5555} and I_{6300}/I_{5577} are given for different currents varying between 100 and 230 mA. The intensity ratios are at any rate very nearly independent of current strength.

Table 6.

The Intensity Ratios I_{5577}/I_{5555} and I_{6300}/I_{5577} as a Function of Discharge Current.

Spectra from Pl. I, Group H corresponding to pure Oxygen ($p = 4{,}5$ mm, tube T_2).

Spectr. No.	Current mA	I_{5577}/I_{5555}	I_{6300}/I_{5577}
1	220	1,9	0,39
2	180	2,0	0,54
3	140	2,5	0,45
4	100	(2,7)	0,44
5	120	2,1	0,50
6	160	2,2	0,40
7	200	2,2	0,32
8	230	1,9	0,37
		Mean 2,1	0,43

The simplest interpretation of this result would be *that the number of O-atoms which in unit time is brought to the upper state corresponding to the forbidden lines is for any pressure and concentration proportional to the number of OI-atoms excited to the upper state corresponding to any of the permitted OI-lines.*

As the electronic density and the density of positive ions increases with current, it should follow that the metastable *OI*-states $^1S_0$ and $^1D_2$ are not essentially effected by collisions with electrons or with positive ions.

It must be remembered however, that the effect produced by such collisions is proportional to the number of electrons or ions per unit volume and to the probability of a collision depriving the atom of the excitation energy. The result found may only mean that the concentration of electrons and ions is too small to show any collision effect on the atoms in the metastable states.

§ 9. THE INFLUENCE OF TUBE DIAMETER ON THE FORBIDDEN AND PERMITTED LINES IN DISCHARGES THROUGH PURE OXYGEN.

The investigation of the influence of the tube diameter on the intensity of a forbidden line, relative to that of a permitted one, was undertaken in pure oxygen, because in that case the interpretation of the results was not complicated by the presence of an inert gas.

The intensity measurements are based on the four series of spectrograms reproduced on Pl. I group I, K, L and M. The series of one group consists of one spectrogram from each of the four tubes. Care was taken that all four spectrograms of the same series should be taken under the same conditions with regard to pressure, discharge current, relative position of spectrograph and discharge tube.

In dealing with these observations it must be remembered that although the total discharge current is the same for all tubes, the current density will be different. If, however, we consider the intensity of the forbidden line 5577 in relation to that of one of the permitted ones, say 5555, the influence of current will be cut out because both lines vary in the same way with current. We have therefore calculated the Ratio $R_n = (I_{5577}/I_{5555})_n$ where (n) is the tube index 1, 2, 3 or 4. In addition we have also calculated the ratio:

$$R'_n = (I_{6300}/I_{5577})_n$$

The results are collected in Table 7. The column headed $\left(\frac{D_n}{D_4}\right)^2$ give the square of the ratio of the diameter D_n of a tube T'_n and the diameter D_4 of tube T'_4.

It appears from the table (7) that $\frac{R_n}{R_4}$ is approximately equal to $\left(\frac{D_n}{D_4}\right)^2$, or:

$$I_{5577}/I_{5555} = K. D^2 \; \ldots . \qquad (13)$$

where K is a function of pressure.

The values of R'_n given in table (7) show that the ratio I_{6300}/I_{5577} is independent of the tube diameter. The deviation shown in the case of tube T'_1 with the smallest diameter is of no significance because in that case the line 6300 was too weak for accurate intensity measurements. This result means that the relation (13) also holds good when I_{5577} is substituted by I_{6300}.

§ 10. A SIMPLE THEORETICAL INTERPRETATION OF EQUATION (13) GIVING THE RELATION BETWEEN I_{5577}/I_{5555} AND THE TUBE DIAMETER.

In trying to give a theoretical interpretation of the results of our intensity measurements, it is first of all a matter of interest to find out how many collisions an oxygen atom makes per. sec. with the gas molecules and the average time it takes an oxygen atom to reach the wall of the tube.

A collision will here be taken in the same sense as in the kinetic theory of gases. We shall consider the more general case where the discharge tube contains a mixture of O_2 and Ne, with partial pressures p_1 and p_2 respectively. Introducing the oxygen concentration:

Table 7.

Variation of the Ratio $R_n = I_{5577}/I_{5555}$ and $R'_n = I_{6300}/I_{5577}$.
With tube diameters of the four tubes indicated T'_n,
$n = 1, 2, 3, 4$.

				R_n/R_4 (n= 4,3,2,1)					$R'_n = I_{6300}/I_{5577}$			
				Pl. I Group					Pl. I Group			
Spectr.	Tube	Tube Diameter D_n mm	$\left(\frac{D_n}{D_4}\right)^2$	I	K	L	M	Mean	I	L	M	Mean
1	T'_4	62,2	1,0	1,0	1,0	1,0	1,0	1,0	0,16	0,22	0,18	0,19
2	T'_3	32,8	0,28	0,45	0,27	0,37	0,26	0,34	0,16	0,21	0,18	0,18
3	T'_2	15,8	0,065	0,058	0,043	0,055	0,047	0,051	0,12	0,25	0,17	0,18
4	T'_1	7,8	0,016	0,029	0,010	0,017	0,010	0,017	(0,23)	(0,27)	(0,23)	(0,24)

$$c = \frac{p_1}{p_1 + p_2} = \frac{p_1}{p} \quad \ldots\ldots\ldots\ldots\ldots\ldots (14_a)$$

we have

$$p_1 = c\,p$$

$$p_2 = (1 - c)\,p = \frac{1-c}{c} p_1 \quad \ldots\ldots\ldots\ldots (14_b)$$

We assume the number of O-atoms to be small compared with the number of O_2-molecules and Ne atoms. Let the number of collisions per sec. between an oxygen atom and an O_2-molecule be Z_{12} and the number of collisions between O- and Ne-atoms Z_{13}, and the total number Z.

Then

$$\left.\begin{aligned} Z_{12} &= \pi\sigma_{12}{}^2 \sqrt{\bar{c}_1{}^2 + \bar{c}_2{}^2}\, n_2 \\ Z_{13} &= \pi\sigma_{13}{}^2 \sqrt{\bar{c}_1{}^2 + \bar{c}_3{}^2}\, n_3 \end{aligned}\right\} \quad \ldots\ldots\ldots (15)$$

σ_{12} is the centre distance $O - O_2 = 3{,}1 \times 10^{-8}$ cm

σ_{13} » » » » $O - Ne = 2{,}6 \times 10^{-8}$ »

The mean velocity $\bar{c} = K \sqrt{\frac{T}{M}}$ cm/sec

where $K = 1{,}455.10^4$

The number of molecules per cm³, $n = \frac{p}{RT} N$

Introducing the values of ($\bar{c}$) and (n) into equations (15) we get:

$$Z_{12} = Z_0\, p_1$$

$$Z_{13} = Z_0\, \varepsilon p_2$$

$$Z = Z_0 (p_1 + \varepsilon p_2) = Z_0 \left(1 + \varepsilon \frac{1-c}{c}\right) p_1 \ldots (16_a)$$

$$Z_0 = \frac{\pi}{R} K N \sigma^2_{12} \sqrt{\frac{M_1 + M_2}{M_1 M_2 T}}$$

$$\varepsilon = \left(\frac{\sigma_{13}}{\sigma_{12}}\right)^2 \sqrt{\frac{M_2 (M_1 + M_3)}{M_3 (M_1 + M_2)}}$$

The pressure p is supposed to be measured in mm Hg.

Putting $T = 330°$ absolute,
Avogadros number $N = 60{,}6\ 10^{22}$,
The gas constant $R = 6{,}24.10^4$,
$M_1 = 16$, $M_2 = 32$, $M_3 = 20$,

we find

$$Z_0 = 7{,}19.10^6, \quad \varepsilon = 0{,}77 \approx 0{,}8$$

$$Z = 7{,}2.10^6 (p_1 + 0{,}8\ p_2) \ldots\ldots\ldots (16_b)$$

Introducing the total pressure p and the concentration (c), we get:

$$Z = 5{,}75.10^6 \left(1 + \frac{c}{4}\right) p \ldots\ldots\ldots (16_c)$$

In table 8 the values of Z_{12} and Z_{13} are given for some partial pressures varying from 0.1 = 10 mm Hg.

Table 8.

Number of Collisions per sec. = table value × 10⁶.

p. mm Hg	0,1	1	2	3	4	5	10	Collision
Z_{12}	0,72	7,2	14,4	21,6	28,8	36	72	O-O_2
Z_{13}	0,58	5,8	11,5	17,3	23,0	28,8	57,6	O-Ne

Table 9.

Total Number of Collisions from Equation (16_c).
Collisions per sec., Z = table value × 10⁶.

p mm \ c	0	0,015	0,03	0,06	0,12	0,24	0,48
1,5	8,6	8,6	8,7	8,7	8,9	9,1	9,6
3	17,3	17,3	17,4	17,6	17,8	18,3	19,4
6	34,5	34,6	34,8	35	35,5	36.5	38,5
12	69	69,3	69,5	70	71	73	77,5
18	103,5	104	104,5	105	106,5	109,5	116
24	138	138,5	139	140	142	146,5	154,5
30	172,5	173	174	175	177,5	183	193

In table 9, the value of the total number of collisions $Z = Z_{12} + Z_{13}$ is given for the total pressures and concentrations actually used in our experiments.

The rapid increase in the intensity ratio I_{5577}/I_{5555} with increasing tube diameter indicates that an O-atom in one of the metastable states loses its excitation energy by collision with the walls of the tube. The question then arises, whether, on the basis of this assumption, we can give a theoretical interpretation of the way in which this intensity ratio varies with tube diameter.

In a tube of given diameter it will on an average take an oxygen atom in the metastable state a time ϑ to reach the wall. Only during this part of its life-time it has a chance to perform the spontaneous transition, which results in the spectral line considered.

Let the number of oxygen atoms per cm³ in unit time transferred to the metastable state considered, be N_0. Let the probability that a transition from this state takes place to lower ones be A, and the probability for transition to one of these lower states be A_r, then $A = \Sigma A_r$.

Let the probability that an exited O-atom by collision with an oxygen molecule loses its excitation energy without radiation be (α). Let the number of the N_0 excited atoms which after a time (t) from excitation have not lost their excitation energy be N, then in the time between t and $t + dt$ the increase in the number of excited atoms due to transitions will be ($-ANdt$) and that due to collisions ($-N\alpha Z_{12}dt$), and the total increase dN:

$$dN = -(A + \alpha Z_{12})\, N dt = -A'N dt.$$

Z_{12} is the number of collisions per sec. between an O-atom and an O_2-molecule at the pressure considered.

The total number left in the excited state after a time (t) will be:

$$N = N_0 e^{-A't} \ldots\ldots\ldots\ldots (17)$$

If the average time used by an excited O-atom to reach the wall of the tube is ϑ, then the number N_ϑ which in unit time from unit volume strike the wall and lose their excitation energy will be:

$$N_\vartheta = N_0 e^{-A'\vartheta}$$

The number (N_r) which in the time (ϑ) undertake transition to lower states is:

$$N_r = A \int_0^\vartheta N\, dt$$

Introducing the value of N from equation (17) and integrating:

$$N_r = \frac{A}{A'} N_0 \left(1 - e^{-A'\vartheta}\right) \ldots\ldots\ldots (18_a)$$

If ($A'\vartheta$) is a small quantity, we may expand into series and drop 2nd and higher orders, then:

$$N_r = A N_0 \vartheta \ldots\ldots\ldots\ldots (18_b)$$

Introducing the mean lifetime $\tau = \dfrac{1}{A}$

$$N_r = N_0 \frac{\vartheta}{\tau} \ldots\ldots\ldots\ldots (18_c)$$

The measured intensity (I) is proportional to N_r and is given by the equation:

$$I = k \frac{A_r}{A} h \nu N_0 \frac{\vartheta}{\tau} \ldots\ldots\ldots (19)$$

In the case of the green auroral line $\dfrac{A_r}{A}$ is nearly equal to 1. For the red lines 6300 and 6364 it is equal to 3/4 and 1/4 respectively. The average time (t), which an O-atom requires to travel a distance (L) from its starting point, is given by Einstein's equation:

$$t = \frac{\bar{L}^2}{2D} \ldots\ldots\ldots\ldots (20_a)$$

where the coefficient of diffusion (D) is given by the expression:

$$D = \frac{3\,(RT)^{3/2}}{8N\sqrt{2\pi}\,\sigma_{12}} \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}\, \frac{1}{p} \ldots . (21)$$

Using the values of T, R, N, σ_{12}, M_1 and M_2 previously given:

$$t = \frac{\bar{L}^2}{536} p \ldots\ldots\ldots\ldots (20_b)$$

For the long discharge tubes used the average distance travelled by an excited oxygen atom to reach the wall, must be approximately proportional to the radius R of the tube. We have put it equal to 3/2 R. This gives:

$$\vartheta = 4.2 \cdot 10^{-3}\, p \cdot R^2 \ldots\ldots\ldots (20_c)$$

The values of ϑ corresponding to the four tubes and various pressures are given in table 10.

Table 10.

The time (ϑ) taken by an O-atom to travel a distance 3/2 R is equal to table value $\times 10^{-3}$ sec.

Tube	T'_1	T'_2	T'_3	T'_4
R cm / p mm Hg	0,39	0,79	1,64	3,11
0,1	0,064	0,26	1,13	4,06
1	0,64	2,62	11,30	40,62
2	1,28	5.24	22,59	81,25
3	1,92	7,86	33,89	121,87
4	2,55	10,48	45,19	162,49
5	3,19	13,11	56,48	203,11
10	6,39	26,21	112,96	406,23

The pressures corresponding to the experimental results given in table 7 range between 2,3 and 4,2 mm. If $\tau' = 1/A'$ is of the same order of magnitude as τ, it appears from table 10 that the values of ϑ in our experiments are small compared with those of τ'. Thus the equation (18 b) should approximately hold good.

Introducing the value of ϑ into equation (19):

$$I = 4.2\ 10^{-3}\, K h \nu A_r N_0\, p\, R^2 \ldots\ldots\ldots (22)$$

In this equation the quantity N_0 changes in an unknown way from one tube to another. For a given tube at a given pressure we found that the intensity of an oxygen line was proportional to (i^n) where (i) is the discharge current.

We might equally well say that the line intensity is proportional to (j^n) where (j) is current density. This means that $N_0 = N_1 j^n$ where N_1 is independent of current density. This value introduced into eq. (22 a) gives:

$$I = 4.2\ 10^{-3}\ K\ h\ \nu A_r\ N_1 j^n p\ R^2 \ldots\ldots\ldots (22_b)$$

In the case of a permitted line the time (ϑ) required by an oxygen atom to reach the wall is large compared with the lifetime of the excited state, and the influence of the walls on the intensity of such a line is negligible. The intensity I' of a permitted line is expressed by the equation:

$$I' = \frac{A'_r}{A'}\, Kh\nu' N_1' j^{n'} \ldots\ldots\ldots\ldots\ldots (23)$$

When the spectrograms corresponding to I and I' are obtained from the same tube $n = n'$. When the forbidden line is compared with a permitted line on the same spectrograms, we have also $K = K'$ and:

$$\left.\begin{aligned} {}^{I}\!/_{I'} &= 4.2 \cdot 10^{-3}\, \frac{\nu A_r A' N_1 p \cdot R^2}{\nu' A'_r N'_1} \\ {}^{I}\!/_{I'} &= \varphi\,(p)\, R^2 \end{aligned}\right\} \ldots\ldots (24)$$

The equation (24) shows that according to theory the ratio of the intensity of a forbidden OI-line to that of a permitted one, at a given pressure, is proportional to R^2 or to the square of the tube diameter (D^2) in accordance with equation (13), expressing the experimental results.

According to equation (18 c) the number of O-atoms in the metastable state which give spontaneous transition is equal to $N_0 \frac{\vartheta}{\tau}$ where N_0 is the total number of metastable atoms in that state produced per sec.

As the intensity of the forbidden and permitted lines in our experiments is of the same order of magnitude, we see from equations (19) and (23) that: $N_0 \frac{\vartheta}{\tau}$ must be of the same order of magnitude as N'_0, or the number of O-atoms taken to the upper state corresponding to one of the observed permitted lines. This means that N_0 must be of the order $N_0' \frac{\tau}{\vartheta}$ and:

$$N_0/N_0' \text{ should be of the order } \frac{\tau}{\vartheta}$$

The values of ϑ are given in table 10. In the case of the line 5577 (τ) is equal to 0,5 sec. and the ratio τ/ϑ will be of the order $10—10^3$. The lifetime of the ${}^1D_2$ state is 100 sec. and τ/ϑ is of the order $10^3—10^5$.

The number of oxygen atoms which per unit volume in unit time are excited to the ${}^1D_2$ state is larger than the number corresponding to the ${}^1S_0$ state, and the number brought per sec. to any of the forbidden states, is very large compared with the number of OI-atoms taken per sec. to any of the non-metastable states.

This result is most probably to be connected with the velocity distribution of the electrons in the positive column. The number of electrons having energies sufficient for the excitation of the ${}^1D_2$ state is large compared with the number which have sufficient energy to excite the higher states.

The number of collisions Z_w which an excited oxygen atom on an average makes on its way to the wall of the tube, has been calculated by means of the formula:

$$Z_w = Z_{12}\, \vartheta \ \ldots\ldots\ldots\ldots\ldots\ldots\ (25)$$

where Z_w and ϑ are taken from tables 8 and 10 respectively. Table 11 contains the results.

Table 11.

Average Collision Number Z_w = table value × 10^3.

p mm Hg	T'_1	T'_2	T'_3	T'_4
0,1	0,046	0,187	0,814	2,92
1,0	4,61	18,86	81,36	292,5
2,0	18,43	75,46	325,3	1170
3,0	41,47	169,8	732,0	2632
4,0	73,44	301,8	1301	4680
5,0	114,8	472,0	2033	7312
10,0	460,8	.1887,1	8136	29246

In the case of tube T'_4 and a pressure of 4 mm, the average number of collisions (Z_w) is 4,7 10^6. These theoretical considerations are given in order to illustrate in a fairly direct manner the observed influence of the tube dimensions, but they do not claim to give the basis for a general theory. This is evident from the fact that the equations (18 c) and (19) do not contain the term which accounts for the effect of collisions with gas molecules. Consequently the theory cannot account for intensity variations with pressure and concentration. A more general theory will be dealt with later on in the paper.

§ 11. VARIATION OF THE INTENSITY OF OI-LINES WITH PRESSURE AND CONCENTRATION OF THE O_2-NE MIXTURE.

EXPERIMENTAL RESULTS.

The variation of the intensity of the permitted OI-lines with oxygen pressure and concentration differs most essentially from that of the forbidden lines. The intensity was measured for a number of permitted lines, but as they show the same type of variation, we found it sufficient to give the variation of the *OI*-line 5555 A.

As already mentioned a series of spectrograms was taken for each mixture (constant concentration c) and varying total pressure. Within the pressure interval of our experiments, *the intensity of a permitted line diminishes with increase of pressure first very rapidly and then more slowly*.

In fig. 4 a we have listed the observed intensities of the line 5555 as a function of the partial O_2-pressure for O_2-concentrations varying between 1,5 and 12 %. When represented in this way, the observations show that *for a given oxygen pressure, the intensity of a permitted line* is nearly independent of concentration or of the Ne-pressure. This at any rate holds for somewhat small concentrations. All points are approximately represented

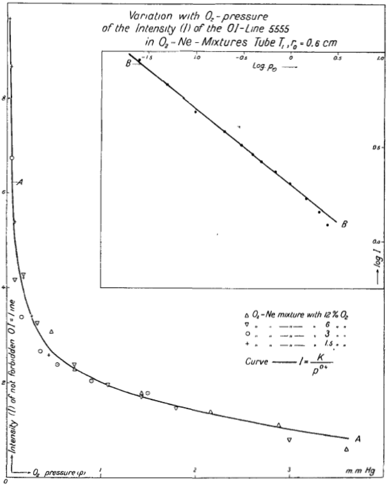

Fig. 4 a.

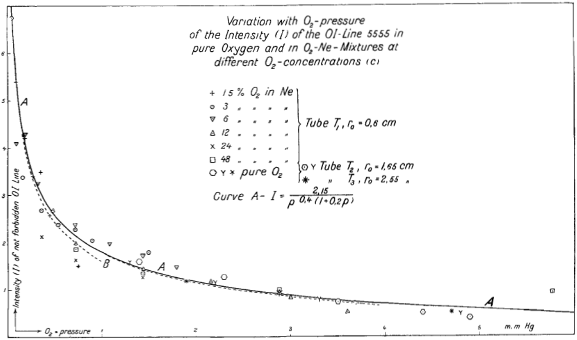

Fig. 4 b.

by a single curve A fig. 4 a. This curve can be expressed by the simple formula:

$$I = K \cdot p_1^{-m} \dots\dots\dots\dots\dots \quad (26)$$

or

$$\log I = A - m \log p_1 \dots\dots\dots\dots\dots (27)$$

where A and m are constants. If $\log I$ is plotted against $\log p_1$, the points are seen to lie on the straight line B fig. 4 a, with a small deviation for the highest O-pressures. A good approximation is found by taking $m = 0,4$.

This result suggests that for a given tube with a given discharge current, the number of oxygen atomes (n), which in unit volume and unit time are brought to one of the ordinary excited states, only depends on the partial oxygen pressure p_1 and only to a very small extent on the Neon-pressure or the concentration, and the variation of (n) with oxygen pressure, should be expressed by the relation:

$$n = k\, p_1^{-0,4} \dots\dots\dots\dots\dots (28)$$

In the diagram (fig. 4 b) the observed intensities of the line 5555 are given for the whole interval of concentrations ranging from 1,5 to 100 % O_2.

The observations are well represented by the curve drawn in full corresponding to a partly theoretical formula:

$$I = \frac{2,15}{p_1^{0,4}\,(1 + 0,2\; p_1)} \dots\dots\dots (29)$$

which will be dealt with later on.

In the diagram fig. 5 a the measured intensities of the forbidden OI-line 5577 are given for various oxygen pressures and concentrations ranging from 1,5 to 48 %.

In fig. 5 b the variation of the intensity of the forbidden line 5577 with pressure is given for pure oxygen. The two curves correspond to tubes of different diameters and different current densities, and are not comparable as regards the absolute values of the intensities.

For a given concentration the observed points show that in this case *the intensity increases with increase of oxygen pressure and has a maximum for a certain value of* $p_1 = p_m$, *which, however, varies with concentration. In the case of the forbidden line the intensity corresponding to a certain oxygen pressure varies very considerably with concentration.* The intensities corresponding to the same concentration define a separate curve in the ($I - p_1$) diagram. The curves drawn in the diagram in fig. 5 a and 5 b are theoretical curves.

The values we obtain for the intensities of spectral lines corresponding to spectrograms taken on different plates may not be exactly

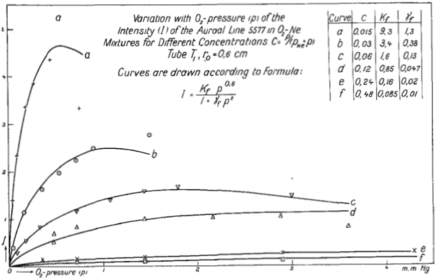

Fig. 5 a.

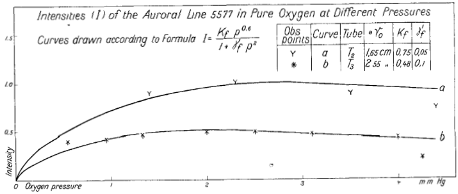

Fig. 5 b.

comparable. The sensitivity curves, even for plates of the same sort, may differ slightly, the position of the tube relative to the collimator may not be exactly the same in all series of experiments, and the discharge conditions may not be the same during the exposure.

Some of these errors should be eliminated if we refer the intensity of a forbidden line to that of a permitted one, taken on the same spectrogram. In other words, the ratio, say $R = I_{5577}/I_{5555}$ should be free from these errors.

The variation of this ratio with oxygen pressure is represented in the diagrams in fig. 6. Fig. 6 a corresponds to the concentrations 1,5—48 %, and fig. 6 b to experiments in pure oxygen. In this case too the points corresponding to a given concentration define a curve of constant concentration. The curves in the diagram are drawn in accordance with a theoretical formula.

In the case of pure oxygen, we have also determined the intensity of the forbidden red line 6300 relative to that of the green line 5577 or the ratio I_{6300}/I_{5577} for pressures varying between 0,55 and 4,0 mm Hg.

The measurements are based on the spectrograms Pl. II group H. Tube diameter 5,1 cm, current 150 mA. The results are given in table 12.

Table 12.

Spectr. No.	1	2	3	4	5	6	7
Pressure mm Hg	0,55	0,95	1,33	2,00	2,5	3,7	4,0
I_{6300}/I_{5577}	0,18	0,19	0,18	0,16	0,16	0,15	0,19

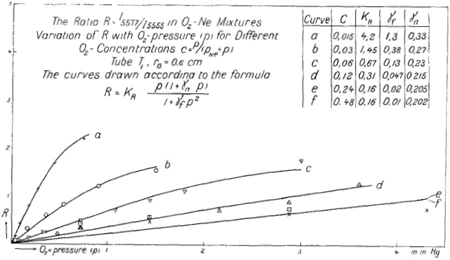

Fig. 6 a.

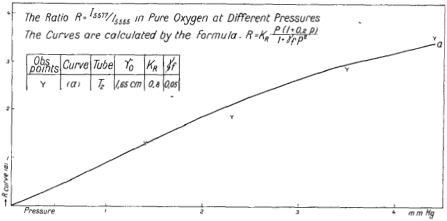

Fig. 6 b.

It appears from table 12 that within the limit of error the intensity ratio I_{6300}/I_{5577} is the same for all pressures. *This means that in our experiments the forbidden red doublet OI* (${}^3P_{2,1}$–${}^1D_2$) *varies with pressure essentially in the same way as the green line OI* (${}^1D_2$–${}^1S_0$).

In the case of the O_2-Ne-mixtures the weak red lines are masked by the strong red Neon-lines and their intensity variations could not be measured from spectrograms taken with our glass spectrograph.

§ 12. THEORY OF THE INTENSITY OF FORBIDDEN AND PERMITTED OI-LINES UNDER THE CONDITIONS OF OUR EXPERIMENTS.

We assume that the current density is constant all over the cross section of the tube and equal to $\frac{i}{\pi r_0^2}$ where (i) is the total current and r_0 the radius of the tube. If so, we may also assume that the number of atoms (N), which per cm³ in one sec. are brought to the metastable state (m) considered, is the same throughout the whole cross section. The number of atoms (q) per cm³ in the (m)-state at any moment is a function of the distance (r) from the tube axis and the time t.

The number of atoms in the m-state which per cm³ disappears each second is $A'q$, where:

$$A' = A + \alpha Z_{12} + \beta Z_{13}$$

where $\frac{1}{A} = \tau$ is the average lifetime of the metastable state, and Z_{12}, Z_{13} are the collision numbers given in equation (15). (α) and (β) are the probabilities that an O-atom in the m-state loses its excitation energy without radiation through a collision with an O_2-molecule and a Ne-atom respectively.

We assume that *all O-atoms at the wall lose their excitation energy (without radiation) by collision with the wall of the tube.* This means that the concentration (q) of O-atoms in the m-state is zero at the boundary surface and that (q) *decreases from a maximum at the axis of the tube to zero at the wall.*

We consider a volume element of length 1 cm and limited by two cylindrical surfaces of radius r and $r_1 = r + dr$. As the concentration (q) varies, the number of excited atoms in this volume element will vary on account of diffusion through the cylindrical boundaries. The number entering the volume element through the cylinder r in one sec. will be:

$$- 2\,\pi r D \frac{dq}{dr},$$

where D is the coefficient of diffusion.

The gain in the number of excited atoms due to diffusion in the volume element is:

$$2\,\pi\,D \left[r_1 \left(\frac{dq}{dr}\right)_1 - r\,\frac{dq}{dr} \right]$$

$$= 2\,\pi\,D \frac{d\left(r\dfrac{dq}{dr}\right)}{dr}\,dr$$

Summing up gain and loss for the volume element we get:

$$2\,\pi\,r\,\frac{dq}{dt}\,dr = 2\,\pi r N dr + {} + 2\,\pi\,D \frac{d\left(r\dfrac{dq}{dr}\right)}{dr}\,dr - 2\,\pi\,r\,A'q\,dr$$

or

$$\frac{dq}{dt} = N - A'q + D\left(\frac{d^2q}{dr^2} + \frac{1}{r}\,\frac{dq}{dr}\right) \;\ldots.\; (30)$$

In the stationary state $\frac{dq}{dt} = 0$ and the variation of q is given by the differential equation:

$$\frac{d^2q}{dr^2} + \frac{1}{r}\,\frac{dq}{dr} - a^2\left(q - \frac{N}{A'}\right) = 0 \;\ldots\ldots\; (31)$$

Where $a^2 = \frac{A'}{D}$.

This well known equation is solved by means of Bessel functions:

$$q = \frac{N}{A'} + C_1 J_0\,(i \cdot r \cdot a) + C_2 Y_0\,(i \cdot r \cdot a) \quad (32)$$

where $i = \sqrt{-1}$.

For $r = 0$, $Y_0 = \infty$, which means that $C_2 = 0$. The boundary condition $r = r_0$, $q = 0$ gives:

$$C_1 = -\frac{N}{A'}\,\frac{1}{J_0(i \cdot r_0 \cdot a)}$$

and

$$q = \frac{N}{A'}\left(1 - \frac{J_0\,(i \cdot r \cdot a)}{J_0\,(i \cdot r_0 \cdot a)}\right) \ldots\ldots\ldots (33)$$

The spectral line considered is supposed to be due to a transition from the metastabel state (m) to a lower state. If the probability of this transition is A_f and the frequency ν_f, the energy emitted from each cm³ is given by the equation:

$$I'_f = A_f\,h\,\nu_f\,q \ldots\ldots\ldots\ldots (34\,\mathrm{a})$$

I'_f, being proportional to q, is a function of (r). The intensity we measure on our spectrograms is proportional to the average energy $\bar{I}_f$ and:

$$\bar{I}_f = A_f\,h\,\nu_f\,\bar{q} \;\ldots\ldots\ldots\; (34\,\mathrm{b})$$

$$\bar{q} = \frac{1}{\pi r_0^2}\int\limits_0^{r_0} 2\,\pi\,r\,q\,dr = \frac{2}{r_0^2}\int\limits_0^{r_0} q\,r\,d\,r$$

$$\bar{q} = \frac{N}{A'}\left[1 - \frac{2}{ir_0a}\,\frac{J_1\,(i \cdot r_0 \cdot a)}{J_0\,(i \cdot r_0 \cdot a)}\right]$$

$$\bar{q} = -\frac{N}{A'}\,\frac{J_2\,(i \cdot r_0 \cdot a)}{J_0\,(i \cdot r_0 \cdot a)} \ldots\ldots\ldots\ldots\ldots (35)$$

Expanding the functions into series and putting $ar_0 = \varrho$:

$$\bar{q} = \frac{N}{A'}\,\frac{\varrho^2}{8}\,\frac{1 + (\frac{1}{2})^2\,\frac{1}{3}\,\varrho^2 + (\frac{1}{2})^7\,\frac{1}{3}\,\varrho^4 + (\frac{1}{2})^9\,(\frac{1}{3})^2\,\frac{1}{5}\,\varrho^6 + \ldots}{1 + (\frac{1}{2})^2\,\varrho^2 + (\frac{1}{2})^6\,\varrho^4 + (\frac{1}{2})^8\,(\frac{1}{3})^2\,\varrho^6 + \ldots}$$

Performing the division of the two polynoms:

$$\bar{q} = \frac{N}{A'}\,\frac{\varrho^2}{8}\,(1 + \tfrac{1}{6}\,\varrho^2 - \tfrac{1}{1152}\,\varrho^4 + \tfrac{1}{34560}\,\varrho^6 + \ldots)^{-1}$$

Dropping all powers higher than the second order and putting

$$\varrho = r_0\,a = r_0\sqrt{\frac{A'}{D}}$$

$$\bar{q} = \frac{N\,r_0^2}{8\,D\left(1 + \frac{1}{6}\,r_0^2\,\dfrac{A'}{D}\right)} \;\ldots\ldots\ldots\; (36)$$

$A' = A + \alpha\,Z_{12} + \beta\,Z_{13}$ and introducing the values of Z_{12} and Z_{13} from eq. 16:

$$A' = A + 10^6 p_1 \left(7.2\,\alpha + 5.8 \frac{1-c}{c} \beta\right) \ldots (37)$$

The coefficient of diffusion D is given in eq. (21). This formula gives:

For O-atoms and O_2-mol., $D_{12} = \frac{270}{p}$

« O-atoms » Ne-atoms, $D_{13} = \frac{420}{p}$

where p is the pressure. Assuming that for a given total pressure p_0 the coefficient of diffusion is a linear function of the oxygen pressure $p_1 = cp_0$, or the concentration c in such a way that $c = 0$ gives $D = D_{13} = \frac{420}{p_0}$ and $c = 1$ gives $D = D_{12} \frac{270}{p_0}$ the diffusion coefficient is given by the equation:

$$D = \frac{420 - 150\,c}{p} = \frac{(420 - 150\,c)\,c}{p_1} \ldots (38)$$

Introducing the expressions for A' (eq. 37) and D (eq. 38) the equation (36) takes the form

$$\bar{q} = \frac{N r_0^2 p_1}{800\,(4.2 - 1.5\,c)\,c} \left[1 + \frac{A + 10^6 p_1 \left(7.2\,\alpha + 5.8 \frac{1-c}{c} \beta\right)}{600\,(4.2 - 1.5\,c)\,c} p_1 r_0^2 \right]^{-1}$$

$$\bar{q} = \frac{N r_0^2 p_1}{800\,(4.2 - 1.5\,c)\,c} (1 + \delta_f p_1 + \gamma_f p_1^2)^{-1} \quad (39a)$$

where:

$$\delta_f = \frac{A r_0^2}{600\,(4.2 - 1.5\,c)\,c}$$

and:

$$\gamma_f = 10^4 \frac{1.2\,\alpha + 0.97 \frac{1-c}{c} \beta}{(4.2 - 15\,c)\,c} r_0^2 \ldots . (39b)$$

A combination of equations (39) and (34 b) gives the expression for the average intensity $\bar{I}_f$ with which the forbidden line is emitted. The intensity I_f of the line as measured from the spectrograms is proportional to $\bar{I}_f$.

Comparing the theoretical formula for I_f with the observed variations of the intensity with pressure and taking into account that for the metastable OI-states $A \gtreqless 2$, we find that δ_f is so small that the term $\delta_f p_1$ is negligible as compared with $\gamma_f p_1^2$, and the intensity of a forbidden line is approximatly given by the formula:

$$I_f = \frac{K_s}{800} \frac{A_f h \nu_f N r_0^2 p_1}{(4.2 - 1.5\,c)\,c\,(1 + \gamma_f p_1^2)} \ldots . (40)$$

In the case of permitted lines the average lifetime of the corresponding upper states is of the order of 10^{-8} sec. and is very short compared with the average time ϑ, which it takes an oxygen atom to reach the wall of the tube. Consequently the diffusion will have practically no influence on the concentration of excited O-atoms in non-metastable states.

The differential equation (30) now reduces to:

$$\frac{dq}{dt} = n - A'_n q$$

(n) is the number of *OI*-atoms brought to a normal excited state per cm³ in unit time. In the stationary state

$$\bar{q} = \frac{n}{A'_n} \qquad (41)$$

The intensity of a permitted line is given by the formula:

$$I_n = \frac{K'_s A_{ni} h \nu_n n}{\Sigma A_{ni} + \alpha_n Z_{12} + \beta_n Z_{13}}$$

$\Sigma A_{ni} = A_n = \frac{1}{\tau_n}$ where τ_n is the average lifetime of the upper state considered

$$I_n = \frac{K_s' h A_{ni} \nu_n n}{A_n \left[1 + \frac{10^6}{A_n} \left(7.2\,\alpha_n + 5.8 \frac{1-c}{c} \beta_n\right) p_1\right]} \quad (42a)$$

§ 13. COMPARISON WITH EXPERIMENTS.

a. Intensity of Permitted Lines.

For small concentrations and oxygen pressures the intensity of an ordinary permitted *OI*-line was found to be approximately independent of concentration and this result suggested that for a given current density $n = n_1 p_1^{-0,4}$ (eq. 28). This expression for (n) introduced into eq. (42) gives:

$$I_n = \frac{K_n}{p_1^{0,4} (1 + \gamma_n p_1)} \ldots\ldots . (42\,b)$$

where:

$$\gamma_n = \frac{10^6}{A_n} \left(7.2\,\alpha_n + 5.8 \frac{1-c}{c} \beta_n\right) \ldots\ldots (43)$$

Applying the equations (42 b) and (43) to pure oxygen we determine $\frac{\alpha_n}{A_n}$ and from applying them to the concentration 0,015 given by the dotted curve B fig. 4 b, we determine β_n.

In this way we found:

$$\frac{\alpha_n}{A_n} = 2.8\ 10^{-8} = \alpha_n \tau_n$$

$$\frac{\beta_n}{A_n} = 3.5\ 10^{-10} = \beta_n \tau_n$$

and

$$\gamma_n = 0.2\left(1 + \frac{1-c}{c}\,\frac{1}{100}\right)$$

As τ_n is of the order 10^{-8} the probability that an OI atom in a normal excited state will lose its excitiation energy by collision with an oxygen molecule, is of the order of magnitude 1. For collisions with Neon atoms, the probability should be very much smaller, which accounts for the fact that the intensity of a permitted line for a given oxygen pressure is nearly independent of concentration.

The curve in the $(I - p_1)$ diagram in fig. 4b has been drawn in accordance with the theoretical formula (42) where we have put $K_n = 2{,}15$, and $\gamma = 0{,}2$.

b. Intensity of Forbidden Lines.

As the intensity of the forbidden and permitted lines varies in the same way with current, it seems legitimate to assume that for a given discharge, the rate of production of metastable states is proportional to that of a normal stationary state. This means that in equation (40) we may put

$$N = N_1 p_1^{-0,4} \qquad (44)$$

and if we want to study the variation of intensity with oxygen pressure for a constant concentration, we have:

$$I_f = \frac{K_f' p^{0,6}}{1 + \gamma_f p_1^2} \ldots\ldots\ldots\ldots (45a)$$

where

$$K_f' = \frac{K_s h A_f \nu_f N_1 r_0^2}{800\,(4.2 - 1.5\,c)c} = \frac{B_f}{(4.2 - 1.5\,c)\,c} \ldots (45\,b)$$

The equation (45) gives a maximum of I_f for

$$p_1^2 = \frac{0{,}429}{\gamma_f} \ldots\ldots\ldots\ldots (46)$$

In the case of pure oxygen and the tube $T_3\,(r_0^2 = 6.5)$ the maximum is found at a pressure of about 2 mm Hg.

$p_{1m} = 2{,}05$ mm gives for $r_0^2 = 6.5$ and $c = 1$, $\gamma_f = 0.103$ and

$$\underline{\alpha = 3{,}6 \cdot 10^{-6}}$$

The spectograms from O_2 — Ne mixtures are taken with tube T_1 ($r_0 = 0{,}6$ cm). If for $r_0 = 0{,}6$ cm, we put $\alpha = 3{,}6 \cdot 10^{-6}$ and adjust γ_f so as to fit in with the experiments in the best possible way we find:

$$\beta = 2{,}87 \cdot 10^{-7}$$

Thus we see that a comparison between theory and experiments has led to a determination of the probability that the metastable ($^1S_0$) state of the O-atom is disturbed by collisions with oxygen molecules or Ne-atoms.

In oxygen 3—4 collisions out of a million disturb the metastable $^1S_0$-state and in Neon only 2—3 collisions out of 10 millions destroy this state.

When the values of α and β are fixed in this way, γ_f is to be calculated by the formula

$$\gamma_f = \frac{43.2 + 2.77\,\frac{1-c}{c}}{(4.2 - 1.5\,c)\,c}\,10^{-3} r_0^2 \ldots (47)$$

Thus for a tube of given radius the value of γ_f can be calculated for any concentration c, and the variation of the intensity I_f with oxygen pressure can be calculated from equations (45).

The intensities of the green line for various concentrations and oxygen pressures are given in the two diagram in fig. 5 a and 5 b. The curves have been drawn in accordance with the formula (45 a). Instead of calculating the intensity factor K_f' (from (45 b), we have for each concentration selected an intensity factor (K_f), which agrees well with the observed points. Thus K_f is to be regarded as the experimental and K_f' as the theoretical intensity factor. We must remember that spectrograms corresponding to different concentrations belong to different series, they are taken on different plates and may not be exactly comparable as regards intensities.

According to equation (45 b) the intensity factor is given by the equation:

$$K'_f = B_f\,[(4.2 - 1.5\,c)c]^{-1}$$

This means that the intensivity factor K_f should be a linear function of $[(4.2 - 1.5\,c)\,c]^{-1}$.

In the diagram in fig. 7 the values of the experimental intensity K_f, used by the construction of the curves fig. 5, are put up as ordinates, and with $[(4.2 - 1.5\,c)\,c]^{-1}$ as abscisse.

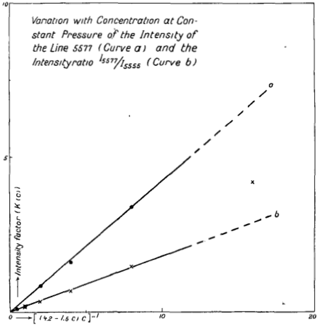

Fig. 7.

Taking into account possible errors we may say that the points fall fairly well on the straight line required by theory. The experimental and theoretical intensity factors K_f and K_f' are given in table 13. K_f' is calculated from eq. 45 b by putting $B_f = 0{,}37$.

Further the values of γ_n and γ_f calculated from equations (43) and (47) respectively are given in table 13.

c. The Influence of the Tube Diameter.

From the equations (40) and (42 a) we find for the ratio $R = I_f/I_n$ the following expression:

$$R = {}^{I_f}\!/_{I_n} = \frac{K_s\,A_f\,\nu_f\,N r_0^2 p_1\,A_n\,(1 + \gamma_n\,p_1)}{800\,(4.2 - 1.5\,c)\,c\,(1+\gamma_f p_1^2) K_s' A_{ni}\,\nu_n\,n}$$

Here we have

$$N = N_0\,p_1^{-0.4}\cdot j^n$$
$$n = n_0\,p_1^{-0.4}\,j^n \qquad (48\,\text{a})$$

For lines on the same spectrogram

$$K_s = K_s'$$

This gives:

$$R = \frac{A_f\,A_n\,\nu_f\,N_0\,p_1\,r_0^2\,(1 + \gamma_n\,p_1)}{800\,A_{ni}\,\nu_n\,n_0\,(4.2 - 1.5\,c)\,c\,(1 + \gamma_f\,p_1^2)} \quad (48\text{b})$$

It appears from equation (47) that γ_f is proportional to r_0^2, and for pure oxygen $c = 1$.

$$\gamma_f = 1.56\cdot 10^{-2}\,r_0^2$$

For a given pressure the variation of the ratio R with the tube radius is given by the expression:

$$R = \varphi\,(p_1)\,\frac{r_0^2}{1+1.56\;10^{-2}\,p_1^2\,r_0^2} \qquad (48\,\text{c})$$

The formula (48 c), applied to our experimental conditions, shows that the ratio $R = I_{5577}/I_{5555}$ is approximately proportional to the square of the tube diameter.

d. The Variation of the Intensity Ratio $R = I_{5577}/I_{5555}$ with O_2-pressure and Concentration.

The equation (48 b) may be written:

$$R = {}^{I_{5577}}\!/_{I_{5555}} = \frac{B_R\,(1 + \gamma_n\,p_1)\,p_1}{(4.2 - 1{,}5\,c)\,c\,(1 + \gamma_f\,p_1^2)} \quad (49\,\text{a})$$

$$R = K'_R\,\frac{(1 + \gamma_n\,p_1)\,p_1}{1 + \gamma_f\,p_1^2} \;\;\ldots\ldots\ldots \;\; (49\,\text{b})$$

where

$$B_R = \frac{A_f A_n \nu_f\,r_0^2\,N_0}{800\,A_{ni}\,\nu_n\,n_0} \ldots\ldots\ldots\ldots (50\,\text{a})$$

$$K'_R = \frac{B_R}{(4.2 - 1.5c)c} \ldots\ldots\ldots\ldots (50\,\text{b})$$

All observations in O_2-Ne-mixtures were made with the same tube ($r_0 = 0{,}6$) and B_R is a constant equal to 0,16. The observed values of the ratio $R = {}^{I_{5577}}\!/_{I_{5555}}$ are set out in the diagrams in fig. 6 a and 6 b for O_2-Ne-mixtures and pure oxygen respectively. The curves are drawn in accordance with the theoretical formula equation (49 b). The factor K_R is determined for each concentration in such a way that the curves represent the observed values in the best possible way. In the case of O_2-Ne mixtures these experimental K_R values are given in the diagram in fig. 6 a and in table 13. The corresponding theoretical values K'_R (cal), calculated from equation (50), are given in the last column of table 13. The relation between the experimentally determined K_R values and $[(4.2 - 1.5\,c)\,c]^{-1}$, which according to theory should be a straight line, is represented in fig. 7 curve (b).

Table 13.

r_0	c	γ_n	γ_f	K_f obs	K'_f cal	K_R obs	K'_R ca
0,6	0,015	0,33	1,3	9,3	6	4,2	2,6
»	0,03	0,27	0,38	3,4	3	1,45	1,3
»	0,06	0.23	0,13	1,6	1,5	0,67	0,65
»	0,12	0,215	0,047	0,85	0,8	0,31	0,33
»	0,24	0,205	0,02	0,16	0,4	0,16	0,17
»	0,48	0,202	0,01	0,085	0,2	0,16	0,10
1,65	1,00	0,200	0,05	0,75		0,80	

e. The Ratio N_0/n_0

The quantities N_0 and n_0 defined by the equations (48 a) represent the number of O-atoms which per cm³ in unit time are excited to a metastable and a normal stationary state respectively. The quantities N_0 and n_0 are referred to the same discharge and the effect of current and pressure is supposed to be eliminated.

According to equation (50) the intensity factor K'_R is given by the equation:

$$\frac{K'_R}{r_0^2} = \frac{A_n \nu_f A_f N_0}{800 A_{ni} \nu_n n_0 c (4.2 - 1.5c)}$$

and

$$\frac{N_0}{n_0} = \frac{800 A_{ni} \nu_n c (4.2 - 1.5c)}{A_n \nu_f A_f} \frac{K'_R}{r_0^2} \quad \text{.. (51 a)}$$

Applied to the green auroral line $\lambda_f = 5577$ and the permitted line $\lambda_n = 5555$, we have:

$\nu_n/\nu_f = 1.004$, $A_f = 2.0$ and putting $A_{ni}/A_n = 0.3$

$$\frac{N_0}{n_0} = 120\, c\, (4.2 - 1.5\, c) \frac{K'_R}{r_0^2} \quad \text{.... (51 b)}$$

According to equation (50 b) $K'_R c\,(4\ 2 - 1.5\,c)$ should be approximately constant and according to equation (48 c), K'_R/r_0^2 should be approximatly independent of the tube-diameter. Thus N_0/n_0 *should be approximately constant in all our experiments and be independent of current, pressure, concentration and tube-diameter.*

The ratio N_0/n_0 has been calculated from the observed intensity-factors K_R given in table 13 for O_2-Ne-mixtures. In this case $r_0 = 0.6$ cm. The results are given in table 14.

Table 14.
The ratio N_0/n_0 for O_2-Ne mixtures.

c	K_R	N_0/n_0
0,015	4,2	88
0,03	1,45	60
0,06	0,67	55
0,012	0,31	50
0,024	0,16	49
0,048	0,16	89

The series represented by the curve in fig. 6 b for pure oxygen corresponds to tube T_2 with a greater radius $r_0 = 1.65$. The intensity factor $K_R = 0.8$ gives $N_0/n_0 = 95$. In the case of the series represented by curve (b), fig. 5 b, the line 5555 was too weak for accurate intensity measurements, so the ratio I_{5577}/I_{5555} could not be found.

In all cases we find that N_0 is much greater than n_0 and thus our theory leads to the result that the number of O-atoms which is brought to the metastable state $^1S_0$ in unit time is on an average about 60—70 times greater than the number which in unit time are taken to the upper state of the permitted line 5555.

This result derived from this more general theory is in agreement with the conclusions we were able to draw from the simpler theoretical considerations previously dealt with in § 10, where also the physical significance of this result was discussed.

SUMMARY.

1. Spectrograms of the forbidden lines *OI* ($^1D_2 - {}^1S_0$) (the green auroral line) and *OI* ($^3P_{2,1} - {}^1D_2$) (the red auroral lines) were obtained in discharges through pure oxygen and mixtures of oxygen and neon. The discharge tubes had a length of 68 cm and diameters varying between 0,78 and 6.22 cm.
2. The relative intensities of the forbidden and of the permitted lines were measured by a photometric method described in the paper.
3. The variation of the line-intensities with tube diameter, discharge current, pressure and oxygen concentration, was studied by

means of spectrograms taken with a glass-spectrograph of fairly high light power. The current varied between 25 and 230 m.A., the total pressure between 1.5 and 50 mm Hg. and the oxygen concentration between 1,5 and 100 %.

4. Spectrograms giving the three forbidden *OI*-lines were also obtained by means of a one metre grating spectrograph. From these spectrograms of large dispersion the wavelengths of the forbidden lines were measured very accurately. The values arrived at (5577,346, 6300,297 and 6363,854) agree very well with the most accurate values previously obtained, and our value for the weak red component may be regarded as the most reliable as yet obtained.

   The energy levels of the metastable *OI*-states were corrected in accordance with the most reliable wavelength values.

   From these spectrograms the intensity ratio I_{6364}/I_{6300} was accurately measured and found to be 0,33, in agreement with theory.

5. The intensity of one of the forbidden lines relative to that of a permitted line, e g. the ratio I_{5577}/I_{5555}, was found to be proportional to the second power of the tube diameter. The measurements refer to discharges in pure oxygen.

6. For a given tube and a given pressure and concentration, the relation between the intensity I of an *OI*-line and the discharge current (i) can be expressed by the formula

$$I = K\,i^n$$

   The exponent (n) is the same for both forbidden and permitted *OI*-lines and equal to 1,67. This result shows that the number of *OI*-atoms, which at a given pressure per unit volume in unit time are brought to a metastable state, is proportional to the number brought to one of the ordinary excited states.

7. For a given O_2-concentration the intensity of a permitted *OI*-line increases as the pressure diminishes — first slowly and gradually more rapidly. At some low pressure below our pressure interval, the intensity has no doubt a maximum. The intensity is approximately a function of the partial pressure of oxygen and is nearly independent of concentration or neon pressure.

8. The variation of the intensity of the forbidden lines with pressure differs very essentially from that of the permitted lines. The intensity first increases with increase of O_2 pressure and reaches a maximum at an oxygen pressure, which varies considerably with the concentration. For a given oxygen pressure the intensity increases when the O_2-concentration diminishes, or with increase of the neon-pressure.

9. The intensity of a forbidden line relative to that of a permitted one, e. g. the ratio I_{5577}/I_{5555}, increases with increase of pressure and will probably reach a maximum, which however in this case may be found at an oxygen pressure outside our interval of observation.

10. The simple law, which we found for the influence of the tube-diameter on the intensity of a forbidden line relative to that of a permitted one, is explained by means of fairly simple theoretical considerations based on the following assumptions:
    a. An O-atom in a meta table state loses its excitation energy without radiation when it strikes the walls of the tube.
    b. The average length of path ($\overline{L}$) which an oxygen atom has to travel from the point of excitation to the wall, is proportional to the radius of the tube.
    c. The average time (ϑ) required for an oxygen atom starting from any point inside the tube to reach the wall, under the conditions of our experiments, is small compared to the average lifetime τ of the metastable states $^1D_2$ and $^1S_0$. The relation $\vartheta = \frac{\overline{L}^2}{2D}$ (D-coefficient of diffusion), applied to the theoretical expression for the intensities of the lines, gives us the relation $I_{5577}/I_{5555} = k\,r_0^2$, where r_0 is the radius of the tube.

11. A more general theory, which gives not merely the influence of the tube diameter, but also the variation of the line intensities with pressure and oxygen concentration,

was worked out. This theory was based on the following assumptions:

a. The number of O-atoms (N) excited to a certain stationary state in unit volume and unit time is the same at all points in the cross section of the tube.

b. In the stationary state the number of atoms (q) per cm³ in a certain metastable state is a function of the distance (r) from the tube axis and is zero at the wall of the tube, or for $r = r_0$.

c. It is supposed that when a metastable state is disturbed by a collision the energy is transfered to the colliding systems. In other words, it is supposed that the probability for transitions to lower states is not influenced by collisions or that the transition probability (A) is independent of pressure.

Taking into account that the number of excited atoms in a volume element is changed through spontaneous transitions and collisions with O_2-molecules and Ne-atoms, through diffusion towards the walls and through the formation of excited atoms by the discharge, we found that in the stationary state the variation of the concentration of excited atoms with the distance (r) from the tube axis is given by the differential equation:

$$\frac{d^2q}{dr^2} + \frac{1}{r}\frac{dq}{dr} - \frac{A'}{D}\left(q - \frac{N}{A'}\right) = 0$$

(D) is the coefficient of diffusion and

$$A' = A + \alpha Z_{12} + \beta Z_{13}$$

$A = \frac{1}{\tau}$, where τ is the average lifetime of the metastable state, Z_{12} and Z_{13} are the numbers of collisions per sec between an excited O-atom and oxygen molecules and Ne-atoms respectively, and (α) and (β) are the probabilities that an O-atom loses its excitation energy through collision with an O_2-molecule or a Ne-atom respectively.

The differential equation is solved by means of Bessel functions. The measured line intensity is proportional to the average intensity ($\bar{I}_f$) across the tube where:

$$\bar{I}_f = A_f h\nu_f \bar{q}$$

$\bar{q}$ is the average value of q, which can be calculated from the known solution of the differential equation.

12. In the case of permitted lines the influence of diffusion is negligible and the average value ($\bar{q}_n$) is equal to $\frac{n}{A_n'}$, where (n) is the number of excited atoms produced per cm³ in one sec.

13. The experimental results lead to the assumption that N is proportional to the number n for a normal excited state, when both correspond to the same discharge. This leads to the equations:

$$n = n_0\, p_1^{-0.4} \cdot j^{1.67}$$
$$N = N_0\, p_1^{-0.4} j^{1.67}$$

where p_1 is the oxygen pressure and (j) the current density. Using these relations the theoretical formula gives a variation of the intensity of a forbidden line with O_2-pressure and concentration, which agrees with experiments, as shown by a number of curves.

14. The adjustment of the coefficients of the theoretical formula to the experimental data leads to a determination of the probability that the excited state is disturbed by collision with a gas molecule. In the case of the forbidden green line OI ($^1D_2 - {}^1S_0$) or the metastable $^1S_0$ state we find:

$$\alpha = 3.6 \cdot 10^{-6}$$
$$\beta = 2.9 \;\; 10^{-7}$$

Thus when an O-atom in the $^1S_0$ state passes through molecular oxygen only one collision out of about 300 000 disturbs the metastable state, so that the atom loses its excitation energy without performing the transition resulting in the emission of the green auroral line.

In the case of neon only one collision in about 3 million produces such an effect.

In the case of the ordinary states connected with the permitted lines, we found:

$$\alpha_n = 2.8 \; 10^{-8} A_n$$
$$\beta_n = 3.5 \; 10^{-10} A_n$$

As the probability of transition from an ordinary state is of the order 10^8, α_n is of the order of magnitude 1, and β_n about a hundred times smaller.

Thus we see that the ordinary excited states of O-atoms are much more sensitive to collision with O_2-molecules and Ne-atoms than a metastable state.

This result has an interesting bearing on the interpretation of certain cosmic light sourses from which forbidden lines are emitted.

15\. The theory leads to the result that the number of O-atoms, N, which in unit volume and unit time are excited to the $^1S_0$-state is about 70 times greater than the number (n) of O-atoms which in the same volume element and in the same time intervall are transferred to the upper state of the permitted line 5555. This result is explained as due to the velocity distribution of the electrons in the positive column of the discharge. The number of electrons having energies sufficiently large to excite the low metastable OI-states is very large compared with the number which are able to excite the higher ordinary non-metastable states.

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EXPLANATION OF PLATE I

Spectrograms taken with the Glass-spectrograph.

On Agfa Isopan ISS plates (not sensitized).

Group	Spectr. No.	Tube	% O_2	Total pressure mm	Current mA	Exp. time min.
A		T_2	100	24	150	5
B	1	T_1	12	30	150	5
,,	2	,,	,,	,,	100	10
,,	3	,,	,,	,,	75	,,
,,	4	,,	,,	,,	55	20
,,	5	,,	,,	,,	25	,,
C	1	,,	,,	24	150	6½
,,	2	,,	,,	,,	100	14
,,	3	,,	,,	,,	75	15
,,	4	,,	,,	,,	55	16
,,	5	,,	,,	,,	25	20
,,	6	,,	,,	,,	125	5
D	1	,,	,,	18	150	5
,,	2	,,	,,	,,	125	6
,,	3	,,	,,	,,	100	10
,,	4	,,	,,	,,	75	,,
,,	5	,,	,,	,,	55	20
,,	6	,,	,,	,,	25	,,
E	1	,,	,,	12	150	4½
,,	2	,,	,,	,,	125	4
,,	3	,,	,,	,,	100	10
,,	4	,,	,,	,,	75	,,
,,	5	,,	,,	,,	55	15
,,	6	,,	,,	,,	25	20
F	1	,,	,,	6	150	7½
,,	2	,,	,,	,,	100	6
,,	3	,,	,,	,,	180	6½
,,	4	,,	,,	,,	125	7
,,	5	,,	,,	,,	125	6½
,,	6	,,	,,	,,	75	10
,,	7	,,	,,	,,	55	20
,,	8	,,	,,	,,	25	,,
G	1	,,	,,	4	125	9½
,,	2	,,	,,	,,	100	12½

Explanation of Plate I

(continued)

Group	Spectr. no.	Tube	% O_2	Total pressure mm	Current mA	Exp. time min.
G	3	T_1	12	4	75	10½
"	4	"	"	"	55	20
"	5	"	"	"	25	"
H	1	T_2	100	4,5	220	10
"	2	"	"	"	180	"
"	3	"	"	"	140	11
"	4	"	"	"	100	"
"	5	"	"	"	120	10
"	6	"	"	"	160	10½
"	7	"	"	"	200	10
"	8	"	"	"	230	"
I	1	T'_4	100	2,3	150	30
"	2	T'_3	"	"	"	6
"	3	T'_2	"	2.7	"	4
"	4	T'_1	"	2,3	"	1¼
K	1	T'_4	"	3,2	"	45
"	2	T'_3	"	"	"	10
"	3	T'_2	"	"	"	3
"	4	T'_1	"	"	"	2
L	1	T'_4	"	4,2	200	45
"	2	T'_3	"	"	150	"
"	3	T'_2	"	"	"	"
"	4	T'_1	"	"	"	15
M	1	T'_4	"	3,8	"	70
"	2	T'_3	"	"	"	11¼
"	3	T'_2	"	"	"	2
"	4	T'_1	"	"	"	"

EXPLANATION OF PLATE II

Spectra taken with the Glass-spectrograph.

On Agfa Isopan ISS plates (not sensitized)

Group	Spectr. No.	Tube	% O_2	Total Pressure mm	Current mA	Exp. time min.
A	1	T_1	48	15,5	150	40
,,	2	,,	,,	12	,,	,,
,,	3	,,	,,	6	,,	35
,,	4	,,	,,	3	,,	40
,,	5	,,	,,	1,5	,,	,,
B	1	,,	24	25	,,	30
,,	2	,,	,,	18	,,	,,
,,	3	,,	,,	12	,,	,,
,,	4	,,	,,	6	,,	25
,,	5	,,	,,	3	,,	30
,,	6	,,	,,	1,5	,,	35
C	1	,,	6	50	,,	15
,,	2	,,	,,	30	,,	,,
,,	3	,,	,,	24	,,	,,
,,	4	,,	,,	18	,,	9½
,,	5	,,	,,	12	,,	10
,,	6	,,	,,	5,5	,,	6½
,,	7	,,	,,	3	,,	3½
,,	8	,,	,,	1,5	,,	2¼
D	1	,,	3	50	,,	12
,,	2	,,	,,	30	,,	13½
,,	3	,,	,,	24	,,	10½
,,	4	,,	,,	18	,,	8
,,	5	,,	,,	12	,,	5½
,,	6	,,	,,	5,4	,,	4
,,	7	,,	,,	1,5	,,	2
E	1	,,	1,5	50	,,	10½
,,	2	,,	,,	30	,,	6
,,	3	,,	,,	24	,,	4¼
,,	4	,,	,,	18	,,	4½
,,	5	,,	,,	12	,,	4
,,	6	,,	,,	6	,,	2
,,	7	,,	,,	3	,,	1
,,	8	,,	,,	1,5	,	½

Explanation of Plate II

(continued)

Group	Spectr. No.	Tube	% O_2	Total pressure mm	Current mA	V	Exp. time min.
F	1	T_2	100	6,4	300	1510	32½
,,	2	,,	,,	4,7	,,	1985	51
,,	3	,,	,,	3,0	,,	1920	45
,,	4	,,	,,	1,9	,,	1625	,,
,,	5	,,	,,	0,9	,,	1215	,,
G	1	,,	,,	6,7	178	1960	15
,,	2	,,	,,	5,3	176	2150	,,
,,	3	,,	,,	4,4	178	1990	12½
,,	4	,,	,,	3,5	180	1750	15
,,	5	,,	,,	2,3	187	1440	,,
,,	6	,,	,,	1,4	191	1220	,,
,,	7	,,	,,	2,9	184	1625	,,
,,	8	,,	,,	4,9	178	2050	,,
,,	9	,,	,,	6,2	176	2050	,,
,,	10	,,	,,	7,5	192	1100	,,
H	1	T_3	,,	0,55	150	1100	,,
,,	2	,,	,,	0,95	,,	1250	16
,,	3	,,	,,	1,33	,,	1485	14
,,	4	,,	,,	2,00	,,	1705	13
,,	5	,,	,,	2,50	,,	1790	14
,,	6	,,	,,	3,10	,,	1888	15
,,	7	,,	,,	4,0	,,	1945	17
,,	8	,,	,,	4,25	,,	1900	12
,,	9	,,	,,	4,35	,,	1830	46

EXPLANATION OF PLATE III

Spectrograms taken with 1 m's grating spectrograph.

On Agfa Isopan ISS plates sentized with NH_3

Spectr. No.	Tube	% O_2	Total pressure mm	Current mA	Exp. time hours
a	T_2	100	2,5	175	40
b	,,	,,	3	150—180	150
c	,,	,,	,,	,,	193
d	,,	,,	3—4	200	178
e	,,	ca. 80	2	,,	198

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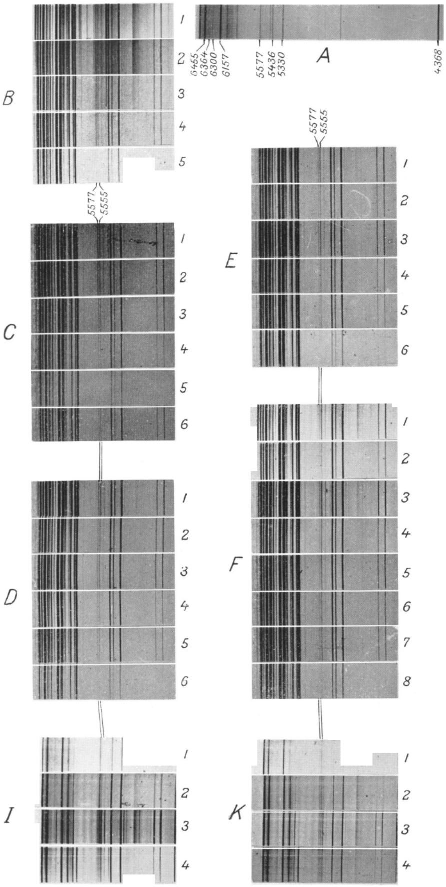
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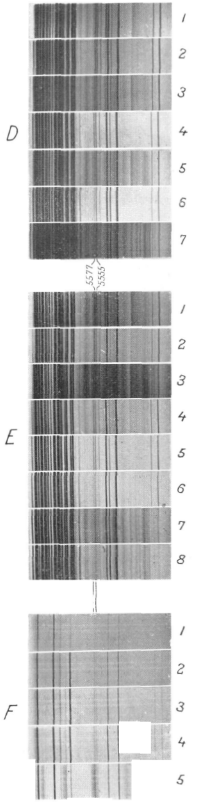
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PLATE III