REVIEWS OF

MODERN PHYSICS

VOLUME 5 OCTOBER, 1933 NUMBER 4

Dispersion in Electrically Excited Gases

RUDOLF LADENBURG, *Princeton University*

CONTENTS

I. GENERAL CONSIDERATIONS 243
II. TRANSITION PROBABILITIES AND LIFETIME OF NEON LEVELS 244
III. POPULATION OF EXCITED LEVELS IN THE POSITIVE COLUMN, STATISTICAL EQUILIBRIUM BETWEEN DIFFERENT LEVELS, RELATION TO ELECTRON TEMPERATURE .. 248
IV. INFLUENCE OF HIGHER CURRENTS UPON THE DISPERSION OF EXCITED GASES AND THE EFFECT OF NEGATIVE DISPERSION 253
V. THE STATISTICAL EQUILIBRIUM BETWEEN THE *s* AND *p* STATES OF NEON 255

I. GENERAL CONSIDERATIONS

IN the neighborhood of an absorption frequency of a rarefied gas, but outside the region of absorption, the refractive index is given by an expression of the form

$$n-1=(\epsilon^2/2\pi m)\cdot[F_{kj}/(\nu_{kj}^2-\nu^2)].$$

See for example the report of Korff and Breit on dispersion.[1] Thus measurements of anomalous dispersion in this region permit the calculation of the quantity F_{kj} which from quantum theoretical considerations is given by [1a]

$$F_{kj}=N_j\cdot A_{kj}\frac{g_k}{g_j}\frac{mc^3}{8\pi^2\epsilon^2\nu^2{}_{kj}}\left(1-\frac{N_k}{N_j}\frac{g_j}{g_k}\right)$$
$$\equiv N_j\cdot f_{kj}(1-Q_{kj}). \quad (1)$$

In these equations j is the lower and k the upper level of the spectrum line under investigation, N_j and N_k are the numbers of atoms per cc in these levels, g_j and g_k the statistical weights, ν_{kj} the frequency of this line and A_{kj} its transition probability. Therefore if the ratio in parenthesis

$$Q_{kj}\equiv N_k g_j/N_j g_k \quad (2)$$

is small compared with 1 and if N_j is known, as is usually the case with gases or vapors in the normal state at known pressure and temperature, one can calculate from the measurement of anomalous dispersion the so-called strength

$$f_{kj}\equiv A_{kj}\cdot(g_k/g_j)\cdot mc^3/8\pi^2\epsilon^2\nu_{kj}^2 \quad (3)$$

and the transition probability A of this line. Experiments in the neighborhood of the resonance lines of Na[2] and of Hg[3] have checked these considerations; for the reciprocal of the so-determined A value coincides with direct measurements of the lifetime T of the resonance level and quantum mechanical calculations of the transition probability for the D lines of Na confirm[4]

---

[1] S. A. Korff and G. Breit, Rev. Mod. Phys. **4**, 471 (1932).

[1a] See also R. Ladenburg, Zeits. f. Physik **48**, 15 (1928).

[2] R. Ladenburg and R. Minkowski, Zeits. f. Physik **6**, 153 (1927).

[3] R. Ladenburg and G. Wolfsohn, Zeits. f. Physik **63**, 616 (1930).

[4] W. Prokofjew, Zeits. f. Physik **58**, 255 (1929); R. Ladenburg and E. Thiele, Zeits. f. physik. Chemie **B7**, 161 (1930).

within the errors of experiment the measured value of A.

For excited gases or vapors where the lower level j of the spectral lines is already an excited level and the population of the atoms in this state N_j is unknown, the determination of the absolute value of A_{kj} by measurement of anomalous dispersion alone is not possible. But it is possible to determine the relative values of A_{kj} for different lines which have the same lower level j and therefore the same number N_j, but have different upper levels k. Such experiments have been carried out for the Balmer lines of hydrogen,[5] and it has been mentioned in the report of Korff and Breit,[1] that the so-determined ratio of A for H_α and H_β coincides with quantum mechanical calculations of this ratio.

Further experiments of similar kind have been carried out with He, Ne and Hg by investigation of the positive column of these gases.[6] Especially in the case of neon excited by direct current the relative f and A values of a great number of lines were determined in this way.

Such determinations are only possible as we have seen in the discussion of Eq. (1), if Q (Eq. (2)) is small compared with unity. This condition can be tested by using the method of "reversal temperature" usually applied to measure flame temperatures. Hedwig Kohn[7] has shown that this method may be used to measure the relative number of excited atoms in any luminous gas. Light from a source giving a continuous spectrum—a black body or a carbon arc or an incandescent lamp—is passed through the luminous gas and analyzed by a spectrograph of high dispersion. The resulting spectrum will show the spectral lines of the gas either as dark or as bright lines depending on whether the black temperature of the source is above or below a critical temperature T_r called the *reversal temperature,* at which the lines just disappear against the continuous background. If there is statistical equilibrium for the different excited states in the gas corresponding to a common temperature, all lines reverse at the same temperature, but in general they do not. Each line has its own characteristic reversal temperature. The length of path, the strength of absorption and the resolution of the spectrograph influence the accuracy of the setting, but not the value of T_r. The only assumption is, that the luminous gas layer passed by the rays of the light source is uniform and that the ratio N_k/N_j of the population of the two states belonging to the line investigated has a definite value along the light path. This ratio or rather the ratio Q of Eq. (2) is given as Hedwig Kohn has shown[7] by an equation identical in form with Boltzmann's equation

$$Q_{kj}=\exp\left[-(\mathcal{E}_k-\mathcal{E}_j)/KT_r\right] \qquad (4)$$

because the disappearance of the line against the continuous background means that every volume of the gas absorbs as much radiation energy as it emits. Therefore

$$N_kA_{kj}h\nu_{kj}=(N_jB_{jk}-N_kB_{kj})u_{kj}h\nu_{kj},$$

where u_{kj} is the radiation density of the light source for the frequency ν_{kj}, A and B are the Einstein coefficients of transition probability for emission and absorption.[8] As T_r is the *black* temperature of the light source, u_{kj} is given by Planck's law

$$u_{kj}=8\pi h\nu^3/c^3[\exp\,(h\nu/KT_r)-1]. \qquad (5)$$

By reversing the considerations applied by Einstein[8] in deriving Planck's law, Eq. (4) follows immediately.

II. Transition Probabilities and Lifetime of Neon Levels

The following investigations deal mostly with the red-yellow lines of neon corresponding to the transitions $s-p$. As shown in Fig. 1 the first excited levels of neon are four s levels s_5, s_4, s_3 and s_2 (${}^3P_2$, ${}^3P_1$, ${}^3P_0$ and ${}^1P_1$) which are rather close together, s_5 and s_3 being metastable while s_4 and s_2 combine with the normal level p_0 and give the ultraviolet resonance lines 743 and 736A. The combination of these four s levels with the ten p levels $p_{10}\cdots p_1$ (${}^1S_0$, ${}^3S_1$, ${}^1P_0$, ${}^3P_{012}$, ${}^1D_2$, ${}^3D_{123}$) give rise to about thirty spectral lines

---

[5] Agathe Carst and R. Ladenburg, Zeits. f. Physik **48**, 192 (1928).

[6] R. Ladenburg, H. Kopfermann and Agathe Carst, Sitzungsber. d. Preuss. Akad. d. Wiss. 1926, p. 256; see also reference 9.

[7] H. Kohn, Phys. Zeits. **29**, 49 (1928); **33**, 957 (1932).

[8] A. Einstein, Phys. Zeits. **18**, 121 (1917).

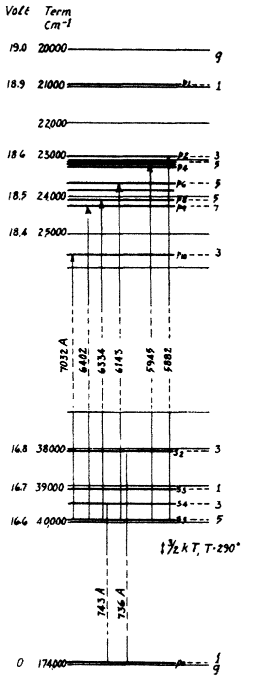

Fig. 1. Term scheme of neon.

which are responsible for the red-yellow light of neon sign lamps. The anomalous dispersion near these lines has been very thoroughly investigated by Ladenburg and his collaborators.[9] They excited tubes of 50 and 80 cm length and of 8 to 10 mm diameter by means of a 20 kv d.c. generator with currents between 0.1 and 700 m.a. The electrodes were large nickel cylinders, mounted in side tubes. The long positive column of luminous gas ("plasma") is very uniform, but when investigated with a rotating mirror it usually shows running striations ("laufende Schichten"). To give reliable results the tubes and the electrodes have to be very thoroughly outgassed and the gas investigated (helium, neon, argon, etc.) has to be very clean, especially free from hydrogen. The light of an arc lamp used as light source is divided by the first plate of a Jamin interferometer[10] into two beams, one of them penetrating the long luminous column, the other an evacuated tube of the same length. The two coherent beams are united by the second plate of the interferometer, and the interference fringes produced are focussed upon the slit of a spectrograph furnished with a large Michelson plane grating which gives a dispersion of 3A per mm in the 3rd order. The continuous spectrum upon which are superimposed the bright lines of the excited gas, is traversed by horizontal interference fringes (Fig. 2), or by oblique fringes if a plane parallel compensating plate is introduced in the beam penetrating the evacuated tube. On both sides of the spectral lines the horizontal fringes are bent off corresponding to the rapid change of the refractive index (Puccianti method) and the oblique fringes show the "hooks" according to Rogestwensky's method.[10] The wave-length distance between the two hooks outside a spectral line allows one in a simple way to calculate the F value (Eq. (1)) of the line.[10] In neon gas one gets these effects near some lines even at currents as low as 1 m.a. because the population of the metastable s_5 and s_3 levels is sufficiently high at these currents. Fig. 2 shows some pictures of anomalous dispersion and of the

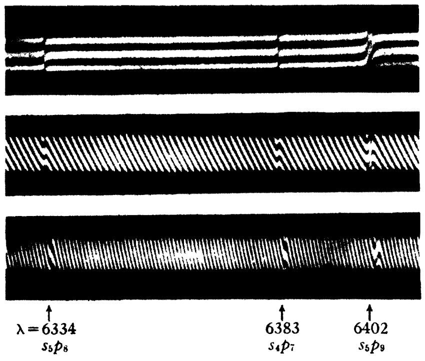

Fig. 2. Pictures of anomalous dispersion near some neon lines.

---

[9] See the papers of R. Ladenburg, Zeits. f. Physik **48**, 15 (1928) (I); R. Ladenburg and H. Kopfermann, Zeits. f. Physik **48**, 26 and 51 (1928) (II and III), Zeits. f. Physik **65**, 167 (1930) (V); R. Ladenburg and S. Levy, Zeits. f. Physik **65**, 189 (1930) (VI). They will be cited as reference 9, I . . . VI.

[10] See report of Korff and Breit (reference 1) p. 482, etc., Fig. 5.

TABLE I. *Relative A and f values for the s–p lines of neon.*

Wave-length	Term	g_p	A	f	Wave-length	Term	g_p	A	f
5882	s_5p_2	3	0.37	0.06_7	6030	s_4p_2	3	~0.15	~0.06
5945	s_5p_4	5	0.29	0.09	6074	s_4p_3	1	1	0.14
5975	s_5p_5	3	~0.16	~0.03	6096	s_4p_4	5	0.30	0.22
6143	s_5p_6	5	0.56	0.18_6	6128	s_4p_5	3	<0.07	<0.03
6217	s_5p_7	4	0.25	0.05	6304	s_4p_6	5	0.12	0.09
6334	s_5p_8	5	0.22	0.12_5	6383	s_4p_7	3	0.53	0.26
6402	s_5p_9	7	1	0.50_0	6506	s_4p_8	5	0.44	0.36
7032	s_5p_{10}	3	0.56	0.14_5	7245	s_4p_{10}	3	0.23	0.14
				$\Sigma f=1.19$					$\Sigma f=1.30$
6163	s_3p_2	3	0.62	0.42	5852	s_2p_1	1	1	0.22
6266	s_3p_5	3	1	0.68	6598	s_2p_2	3	0.34	0.28_5
6532	s_3p_7	3	0.54	0.41	6678	s_2p_4	5	0.32	0.46
				$\Sigma f=1.51$	6717	s_2p_5	3	0.33	0.28_5
					6929	s_2p_6	5	0.28	0.43
					7174	s_2p_8	5	0.06	0.10
									$\Sigma f=1.78$

hooks near the lines 6402 (s_5p_9), 6383 (s_4p_7) and 6334 (s_5p_8) at a current of about 50 m.a. As a matter of fact, the population in the lower level of a spectral line must be rather high in order to give the effect of anomalous dispersion. That is the reason this effect is observable only in relatively few cases. That in Fig. 2 the line s_4p_7 belonging to the unstable lower level s_4 shows anomalous dispersion can be understood as being due to the interchange of energy between the atoms in s_5, s_4 and s_3 states because the mean energy of the neon atoms at room temperature (0.04 volt) is of the same order as the energy difference between these levels. Moreover the population in the unstable level s_4, though decreasing by radiation of the line 743, is continually being replenished by strong reabsorption of this radiation.[11] Therefore it remains of the same order of magnitude as that of the metastable states s_5 and s_3 and is hence called "quasi metastable." The energy of the level s_2 is 0.23 volt higher than that of s_5 and behaves therefore in a somewhat different way (see Fig. 6, Section III). It is possible however at higher currents[12] to measure the anomalous dispersion of the lines belonging to this level.

Simultaneous measurements of the reversal temperature of the lines with the carbon arc as light source showed[13] that the ratio Q of Eq. (1) was small compared with unity, as long as the current through the gas was below 100 m.a. Therefore, the statistical weights for all s and p levels being known, the relative values of F_{kj} of different neon lines[14] belonging to the same s and to different p levels give the relative f_{sp} and consequently the relative A_{sp} values (Eq. (3)).

Table I contains the so-determined relative A values for the different sp lines[15] arranged according to their common lower levels $s_5\cdots s_2$. The table contains also the absolute f values as will be explained below.

By combining these experiments on anomalous dispersion with measurements of the ratio of the true intensity of lines belonging to the *same upper*, but to *different lower levels*, it is possible to calculate also the relative A and f values of the lines with different lower levels, for the intensity of a spectral line k–j of a gas layer of infinitesimal thickness (its "true" intensity) is

$$II_{kj}\equiv N_k\cdot A_{kj}\cdot h\nu_{kj}. \tag{6}$$

Usually the light intensity of a luminous gas layer of finite length l is *not* simply l times as large, but is influenced by the self-absorption of the light in the gas itself; this is especially true in the case of the s-p lines of excited neon in which the population of the s levels and the corresponding self-absorption is high. As a matter of fact, the absorption of these lines is so strong that it is nearly impossible to get completely rid

---

[11] Reference 9, II, p. 42.

[12] Reference 9, VI, p. 198.

[13] Reference 9, II, p. 38.

[14] The measurements for different lines have to be made of course at the same current.

[15] The largest A value for a definite s level is put as unity.

of it. Dorgelo[16] has tried to get "true" intensity ratios of the neon lines undisturbed by self-absorption, by using small amounts of hydrogen in the neon discharge.[17] Meissner and Dorgelo have shown that hydrogen destroys the metastable neon atoms and therefore the absorption and also the anomalous dispersion. That is why for such investigations the gas has to be freed especially from hydrogen. Ladenburg and Levy[18] have given another method for calculating "true" intensities, by taking the absorption into account and correcting the measured intensities correspondingly. This is only possible of course if the intensity distribution of the emission and absorption coefficient is known. In the positive column of a neon discharge this intensity distribution is determined by the Doppler-effect[18] (compare Fig. 3 taken from the paper of Ladenburg-Levy), and the authors have shown that the intensity of the spectral lines of a finite layer l of the luminous gas is equal to the intensity of an infinitesimal layer multipled by the expression $l \cdot S$ where

$$S = 1 - \frac{C}{2 \times 2^{\frac{1}{2}}} + \frac{C^2}{6 \times 3^{\frac{1}{2}}} - \cdots (-1)^n \frac{C^n}{(n+1)!(n+1)^{\frac{1}{2}}} + \cdots$$

and $C = 2F\epsilon^2 l/\nu_0 m\bar{q}$, $\bar{q}$ being the mean velocity of the atoms. The sum S is given in a table in the paper of Ladenburg-Levy (reference 9, VI) for values of C between 0.1 and 1000. The F values of the neon lines are known from the measurements of anomalous dispersion. By this method the intensity ratios of the lines 6678 (s_2p_4)/5944 (s_5p_4) and of 6598 (s_2p_2)/5882 (s_5p_2) and therefore the ratios of their A values were determined. In this way the A values of all the s_2 lines relative to the A values of the s_5 lines were calculated.[15] In a similar way the A values of the s_4 and s_3 lines relative to the s_5 lines are calculated by using intensity ratios from measurements by Dorgelo given in Table II. The results of these calculations are given in Tables I and III. Table I shows the f values of the different lines reduced to the f value of the line 6402 which is put equal 0.5. In Table III one finds the A values of the neon lines reduced to the absolute A value of the line 6402 (s_5p_9) corresponding to $f = 0.5$. The method for estimating these absolute values of f and A is given in Section III. The abbreviation v.s. in the table signifies that the A value of this line is so small that the anomalous dispersion of this line could not be measured; ? means that the value is not measured and is unknown; 0 means that this combination does not exist, i.e., that its A value is practically zero. The largest A values are those of the resonance line s_5p_9 and the "quasi-resonance" lines s_4p_3 and s_2p_1. The upper levels combine each with one other lower level but the corresponding transition probability is so

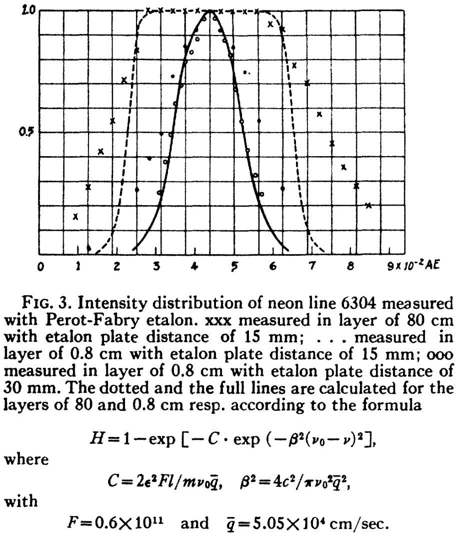

FIG. 3. Intensity distribution of neon line 6304 measured with Perot-Fabry etalon. xxx measured in layer of 80 cm with etalon plate distance of 15 mm; . . . measured in layer of 0.8 cm with etalon plate distance of 15 mm; ooo measured in layer of 0.8 cm with etalon plate distance of 30 mm. The dotted and the full lines are calculated for the layers of 80 and 0.8 cm resp. according to the formula

$$H = 1 - \exp\left[-C \cdot \exp\left(-\beta^2(\nu_0 - \nu)^2\right]\right.,$$

where

$$C = 2\epsilon^2 Fl/m\nu_0\bar{q}, \quad \beta^2 = 4c^2/\pi\nu_0^2\bar{q}^2,$$

with

$$F = 0.6 \times 10^{11} \quad \text{and} \quad \bar{q} = 5.05 \times 10^4 \text{ cm/sec.}$$

TABLE II.

Lines	Series	Intensity ratio
6506/6334	s_4p_8/s_5p_8	100 : 62
6096/5945	s_4p_4/s_5p_4	100 : 62
6163/5882	s_3p_2/s_5p_2	100 : 75
6532/6217	s_3p_7/s_5p_7	100 : 59

---

[16] H. B. Dorgelo, Physica **5**, 90 (1925); H. B. Dorgelo and W. de Groot, Zeits. f. Physik **36**, 897 (1926).

[17] Reference 9, III, p. 55.

[18] Reference 9, VI, p. 200.

TABLE III. *A values of neon lines, reduced to the absolute A value for λ6402 (s_5p_9) corresponding to $f=0.5$.*

Terms		$A_{ps}\times10^{-7}$ $^3P_2$ s_5	$^3P_1$ s_4	$^3P_0$ s_3	$^1P_1$ s_2	$\Sigma_s A\times10^{-7}$	$1/\Sigma A=T$
$^1S_0$	p_1	0	v.s.	0	12.8	13	$<0.8\times10^{-8}$
$^3P_1$	p_2	2.1_2	~1.2	2.4_4	4.3_2	10	1.0
$^3P_0$	p_3	0	7.8	0	v.s.	8	1.2_5
$^3P_2$	p_4	1.7	2.3_8	0	4.1_0	8.2	1.2
$^1P_1$	p_5	~0.9	<0.6	3.8_4	4.1_7	<9.5	>1.05
$^3D_2$	p_6	3.2_5	0.9_3	0	3.5_6	7.7	1.3
$^3D_1$	p_7	1.4_6	4.1_7	2.1_4	v.s.	7.8	1.3
$^1D_2$	p_8	2.0_7	3.4	0	0.8_6	6.3	1.6
$^3D_3$	p_9	5.7_8	0	0	0	5.8	1.7
$^3S_1$	p_{10}	3.2_4	1.8	?	?	>5.0	<2.0
$\Sigma_p A\times10^{-7}=$		20.5	22.3	8.4	29.7_5		

small that it could not be measured. Furthermore, Table III gives the sum ΣA of all lines belonging to the same upper level. The reciprocal value of this sum is equal[19] to the lifetime T of the upper levels $p_1, p_2 \cdots p_{10}$. The table shows that this lifetime varies from 0.8×10^{-8} up to 2×10^{-8} for the different p levels. The lifetime increases systematically as the energy of the level decreases. The small irregularities are within the accuracy of the measurements which is of the order of 10–15 percent.

III. Population of Excited Levels in the Positive Column, Statistical Equilibrium Between Different Levels, Relation to Electron Temperature

The same measurements of anomalous dispersion and of "true" intensity of the neon lines make it possible to calculate the relative population of the different excited levels of neon. This follows at once from the equations

$$F_{kj}=N_jf_{kj}=N_jA_{kj}(g_k/g_j)\cdot mc^3/8\pi^2e^2\nu_{kj}^2 \quad \text{(1a)}$$

and

$$H_{kj}=N_k\cdot A_{kj}\cdot h\nu_{kj}. \quad (6)$$

The first of these equations contains the assumption that the population of the upper level is so small that the ratio $Q\equiv N_kg_j/N_jg_k$ can be neglected (see Section I). If we compare two lines with the same upper level (let us say p_2) and with different lower levels (say s_5 and s_3) we get from the intensity ratio of these lines the ratio of their A values and from measurements of their anomalous dispersion the ratio of their F values, thus we get the ratio $N_{s_5} : N_{s_3}$.

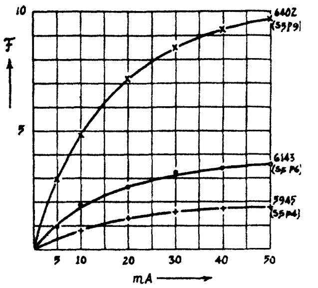

FIG. 4. Increase of F values of different s_5 lines with the current.

While the "true" intensity ratio of two lines with the same upper level is independent of the current, the F values and their ratio for lines with different lower levels does depend rather strongly upon the current flowing through the positive column. Fig. 4 shows this change[20] for some lines of neon with currents between 5 and 50 m.a. Before proceeding to the results of measurements of the population of excited levels we have therefore to consider how and why the anomalous dispersion and the F values depend upon the current. The increase of the F values with current could be produced, according to Eq. (1a), either by an increase of the population of the lower level of the line, or by an increase of its A value, the transition probability. The values of A_{kj} are properties of the atoms and a

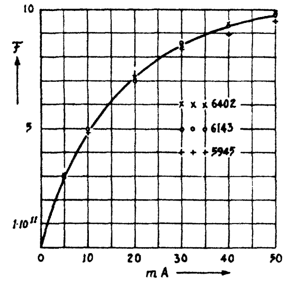

FIG. 5. F values of different s_5 lines as functions of current reduced to the same scale.

---

[19] As pointed out by R. Ladenburg, Zeits. f. Physik 4, 455 (1921).

[20] In the German papers the notation 𝔑 of the ordinates of the Figs. 4, 5 . . . stands for our F.

change of these values with the current is very improbable. Theoretically very strong electric fields might influence the A values, but in the experiments here described such an effect does not seem to be present, for if we reduce to the same scale the F values of the different lines of Fig. 4 which belong to the same lower level s_5, the reduced values coincide (see Fig. 5), consequently it must be the population N_{s_5} (common to the different lines) which changes with the current. We know that with increasing current the number of electrons increases and that these electrons, if fast enough, excite the atoms of the gas by collisions of the "first kind," either directly or through the p levels which are much more easily excited than the s levels.[21] On the other hand electrons colliding with excited atoms will destroy them by collisions of the "second kind." The excited atoms are also destroyed by collisions with the walls or with other atoms or by spontaneous radiation, but on the other hand, as was mentioned above, the re-absorption of radiation can lift the atoms from the normal level to an excited one, if this is not metastable. In the steady state the resultant rate at which the atoms are raised to a particular level must equalize the rate at which the atoms in this level are destroyed. To a first approximation the number of atoms excited and destroyed by collisions with electrons is proportional to the current. But with higher currents higher powers of the current have also to be taken into account, because of cross interactions between atoms already excited by electron impact. Therefore in the steady state the population of a definite level characterized by the index j can be approximately represented by[22]

$$N_j=(AI+BI^2)/(CI+DI^2+E). \qquad (7)$$

Here I is the current and A, B, C, D and E are positive constants independent of the current which contain the probability of exciting and destroying the atoms j by the different processes mentioned above. The term E which does not depend upon the current is due to the destruction of the excited atoms by spontaneous radiation and by collisions with the walls of the tube or with other atoms. There is no corresponding term for exciting the atoms.

With small current the quadratic terms can be neglected and we get the simple equation

$$N_j=\alpha I/(\beta I+1), \qquad (8)$$

where $\alpha=A/E$ and $\beta=C/E$. The reciprocal value of N_j becomes a linear function of $1/I$. This connection was examined by experiments with the different s-p lines of neon (reference 9, II) and it was shown that it holds approximately for currents between 10 and 60 m.a.[23]

Fig. 6 represents the increase of the population of the different s levels with the current up to 60 m.a. at a neon pressure of 1.3 mm. The curves are deduced from the F values of different lines having the same lower level, as these can be represented by the same curve, i.e., by the same function of I, at least up to 60 m.a., as shown above.

We see from this figure that the curves of the population of s_5, s_4, and s_3 are very similar in shape, but that that of s_2 behaves in quite another way, corresponding to our consideration in Section II. The curves of s_5, s_4 and s_3 increase at first rapidly with the current, but this increase slows down and at 50 m.a. a kind of "saturation" is approached, where the population no longer increases with increasing current. This effect which is even more pronounced at higher gas pressures (reference 9, II, Fig. 6), means that in Eq. (8) the term βI becomes large compared with 1, i.e., the number of collisions with electrons destroying the levels becomes large compared with all other destroying factors, such as collisions with the walls of the tube and especially spontaneous radiation. This is obviously a kind of statistical equilibrium between the colliding electrons and the excited atoms.

This approximation of a statistical equilibrium is also shown by the ensemble of the different s states. Above 50 m.a. the ratio of the population of s_5, s_4 and s_3 is 100 : 52.5 : 17.5 (cp. Fig. 6). The ratio of their statistical weights is 5 : 3 : 1, and if the Boltzmann law corresponding to a high "specific temperature," for instance 10,000°, would hold for their population, the

---

[21] See M. I. Druyvesteyn, Zeits. f. Physik **64**, 787 (1930).

[22] Reference 9, VI, p. 178.

[23] The deviations from the linear relation at very small currents are not yet explained satisfactorily.

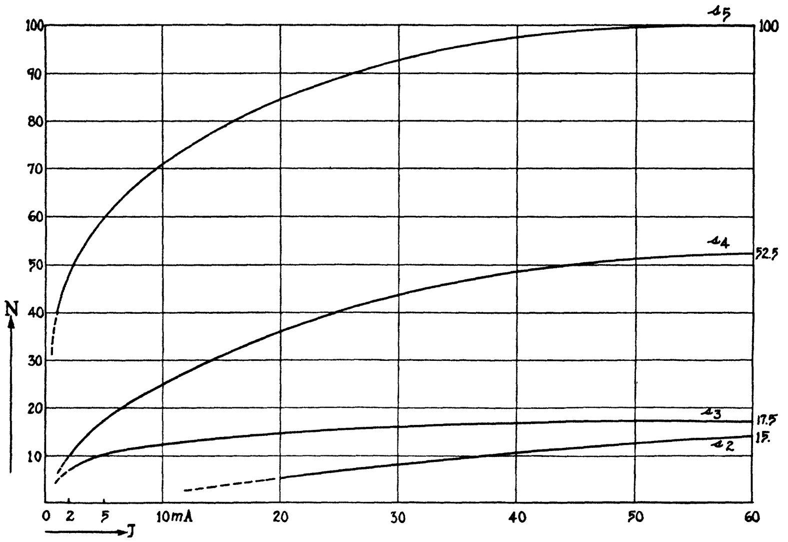

FIG. 6. Increase of population of s levels with current (neon pressure 1.3 mm).

ratio would be 100 : 56 : 18. The population of the s_2 state at the currents used is far from such equilibrium (15 instead of 46) and there is no "saturation" of its population, as we see from Fig. 6. One reason is that the s_2 level lies about 0.2 volt higher than the other three so that the mean energy of the atoms at room temperature is not sufficient for an energy exchange, and besides this, the spontaneous disintegration of the s_2 level by radiation is very high.[24]

Because the s levels lie too near together the measurements of the populations are not exact enough for testing the Boltzmann law and for calculating in this way a "specific temperature." However, under certain conditions, general theoretical considerations show the existence of a statistical equilibrium between excited atoms and electrons and the validity of the Boltzmann law for the excited atoms. It is necessary to assume only that the velocities of the electrons in the plasma have a Maxwellian distribution[25, 26] and furthermore that the excitation to and destruction of excited states are due preponderantly to electron impact, i.e., that the number of such effective electron collisions is so large that they overbalance all other processes of excitation and especially of destruction by spontaneous radiation or by collisions with the walls or with other molecules.

This important result follows immediately[27] by reversing the considerations of Klein-Rosseland.[28] Though it does not seem to be quite self-evident that on account of the partial equilibrium between electrons and excited atoms there is a detailed balance ("microscopic reversibility"[28a]) between every process of excitation and destruction of atoms by electron impact, which would lead at once to the validity of Boltzmann's distribution of the excited atoms corresponding to the electrom temperature, the following simple considerations[27] give the same result: The

---

[24] Its transition probability is about 13 times larger than that of s_4, according to recent unpublished calculations of G. H. Shortley.

[25, 26] As demonstrated for Hg vapor by I. Langmuir and Mott-Smith (Phys. Rev. **28**, 727 (1926), etc.) (see K. K. Darrow, *Discharges in Gases*, 1932) and for Ne by R. Seeliger and R. Hirchert (Ann. d. Physik **11**, 817 (1931)).

[27] See H. Kopfermann and R. Ladenburg, Naturwiss. **19**, 512 (1931).

[28] O. Klein and S. Rosseland, Zeits. f. Physik **4**, 46 (1921).

[28a] Compare Tolman's book on *Statistical Mechanics*, p. 165, 1927.

Maxwelliam distribution means that the number of electrons of energy between E and $E+dE$ is $n(E)dE=C\cdot E^{\frac{1}{2}}\exp(-E/kT_\epsilon)dE$, T_ϵ being the "electron temperature." If E_j and E_k are the energies of two levels of the atom, then the level of higher energy k is excited only by electrons with energy $E''>E_k-E_j$; the corresponding probability being $S_{jk}(E'')$. The energy of electrons after the exciting collision is $E'=E''-(E_k-E_j)$. In a collision of "the second kind" such electrons destroy excited atoms with a probability $S_{kj}(E')$ taking up the energy E_k-E_j. According to Klein and Rosseland[28] there exists the well-known relation between the two probabilities:

$$g_jE''^{\frac{1}{2}}S_{jk}(E'')=g_kE'^{\frac{1}{2}}S_{kj}(E'), \tag{9}$$

g_j and g_k being, as before, the statistical weights of the two atomic levels. Klein and Rosseland derived this relation by assuming a temperature equilibrium between atoms and electrons. But the probabilities S as well as the weights g are properties of the atoms and electrons and do not depend upon the existence of a statistical equilibrium nor do they change generally with outside conditions. The same is true for the transition probabilities. We may therefore apply relation (9) to the processes in the plasma without assuming a statistical equilibrium between atoms and electrons. But we make the important assumption that the current density in the plasma is very high, i.e., that so many collisions of the second kind occur between excited atoms and electrons, that the number of atoms destroyed per second by these collisions is equal to the number excited per second by electronic collisions. Of course the excited atoms are also destroyed by other means as mentioned above, but the number of these processes shall be supposed to be very small compared with the number of collisions of the second kind with electrons. Our assumption is therefore rigorously valid only for very large currents. By equalizing the number of collisions of the first kind and of the second kind we get

$$N_j\int_{E_k-E_j}^{\infty}S_{jk}(E'')\exp(-E''/KT_\epsilon)E''^{\frac{1}{2}}dE''=N_k\int_0^{\infty}S_{kj}(E')\exp(-E'/KT_\epsilon)E'^{\frac{1}{2}}dE'.$$

We substitute on the left-hand side of this equation the variable of integration E'' by $E'=E''-(E_k-E_j)$ and the probability $S_{jk}(E'')$ by $S_{kj}(E')$ according to the Klein-Rosseland relation (9) and get

$$N_j\int_0^{\infty}S_{kj}(E')\exp(-E'/KT_\epsilon)\cdot\exp(-[E_k-E_j]/KT_\epsilon)\cdot g_k/g_jE'^{\frac{1}{2}}dE'$$
$$=N_k\int_0^{\infty}S_{kj}(E')\exp(-E'/KT_\epsilon)E'^{\frac{1}{2}}dE'$$

and therefore

$$N_k/N_j=g_k/g_j\exp(-(E_k-E_j)/KT_\epsilon), \tag{10}$$

i.e., for large currents in the plasma *the ratio of the populations of the two atomic levels corresponds to a statistical equilibrium at the electron temperature.* This result can be tested experimentally, for from the experiments on anomalous dispersion in neon it is possible to calculate to some extent the ratio N_k/N_j.

As stated above, the F values determined by anomalous dispersion give only the product N_jf_{kj}. The absolute value of f can however be estimated by using the f sum rule of Thomas-Reiche-Kuhn:[29]

$$\sum_a f_a-\sum_e f_e=Z, \tag{11}$$

Z being the number of electrons of the atoms. The first sum, characterized by the index a, refers to all possible absorption transitions of the atom in the state considered, the second sum, characterized by the index e, refers to all emission transitions of this state. For the metastable state

---

[29] W. Thomas, Naturwiss. **19**, 627 (1925); W. Kuhn, Zeits. f. Physik **33**, 408 (1925), F. Reiche and W. Thomas, Zeits. f. Physik **34**, 510 (1925).

s_5 of the neon atom the second sum vanishes. By multiplying both sides of Eq. (11) by N_{s_5} we get

$$\sum_a N_{s_5} f_{s_5 a} = \sum_k F_{s_5 k} = Z \cdot N_{s_5}.$$

We have to consider that only one outer electron in the neon atom is efficient in the absorption lines of the state s_5, but that the *f* sum of the inner electrons may be smaller than their number;[30] therefore the *f* sum of a single outside electron may be larger than unity and may even be 2. A further uncertainty arises from the fact that we know the *f* values only for the combination of s_5 with the p_k levels, but not for the higher transitions nor for the adjacent continuum.[31] By taking care of these uncertainties[32] we get for the value of N_{s_5} at the current of 100 m.a. and 1 mm pressure in a tube of 0.8 cm diameter the limits 2.6 and 13.8×10^{12}. The absolute value of f_{6402} is then included between the limits 0.85 and 0.21 (mean value 0.5 ± 0.3 (see Table I))[32a] and from the known population of the normal neon atoms in p_0 state we get for the value of $Q \equiv N_{s_5} g_{p_0} / N_{p_0} g_{s_5}$ the limits 3×10^{-5} and 16×10^{-5}. The corresponding "specific temperature" of the excited s_5 atoms, defined by Eq. (10), becomes therefore 20,200° ±10 percent; for the s_4 and s_3 atoms this temperature is about 300° less, i.e., the same within the limits of experimental error. For higher currents (cp. following sections) the specific temperature is about 400° smaller. We will see there that for higher currents a statistical equilibrium even between higher states is reached corresponding to a similar temperature.

The electron temperature was determined by Seeliger and Hirchert[26] in the positive column of a low voltage arc in neon. They used tubes of 40 and 20 mm diameter without getting an appreciable difference. As the experiments on anomalous dispersion were carried out in tubes of only 8 mm diameter there remains a small uncertainty. The values of Seeliger and Hirchert are contained in Table IV[33] (accuracy 10 percent). For 1 mm pressure the value of the electron temperature at 100 m.a. is therefore about 26,600° and at 300 m.a. about 22,000°. This value is in sufficient agreement with the specific temperature 20,200° ±10 percent, calculated above from the measurements of the population of excited atoms at 1 mm pressure.[34] Moreover with increasing pressure the specific temperature of excited atoms decreases in a way similar to the electron temperature and falls off to about 15,000° at 9 mm pressure where the electron temperature is about 16,000° according to Table IV. The experiments show that the statistical equilibrium of the excited atoms at higher pressure is already reached at lower currents. This can be understood, for with increasing pressure the collisions with the walls which destroy the excited atoms decrease as their rate of diffusion is decreased; on the other hand, the number of slow electrons which are responsible for the collisions of the second kind with excited atoms increases with the pressure if the current is kept constant. Both effects act in the same sense producing the observed fact.

TABLE IV. *Electron temperature in neon as function of pressure and current from measurements of Seeliger and Hirchert.*

Pressure	50 m.a.	100 m.a.	300 m.a.
0.65 mm	33,000°	30,200°	24,400°
0.8	28,600	27,200	22,400
2	25,200	24,800	21,800
4	20,200	20,200	19,800
11	—	16,300	15,100
20	—	—	16,300

F. L. Mohler[35] has investigated the positive column of a caesium discharge; he determined the electron temperature and simultaneously the number of excited atoms. In agreement with our results in a neon discharge he found

---

[30] See R. de L. Kronig and H. A. Kramers, Zeits. f. Physik **48**, 174 (1928).

[31] We know only that the *f* value of the second line of the strongest series s_5–p_9 ($\lambda = 3473$) is very small, certainly smaller than 1/7 of that for 6402. (See Agathe Carst, Zeits. f. Physik **48**, 59 (1928).)

[32] For details of the calculation compare Zeits. f. Physik **65**, 185 (1930).

[32a] The sum of the *f* values for the four *s* levels given in Table I is incomplete according to the foregoing considerations, furthermore there are transitions of emission from s_4 and s_2 to the normal level, the f_e values of which cannot be neglected.

[33] The authors give their values in volts and state that 1 volt corresponds to 7750° ($eV = 3KT/2$).

[34] Recently M. I. Druyvesteyn (Zeits. f. Physik **81**, 571 (1933)), got appreciably higher results than Seeliger and Hirchert, but this discrepancy is not yet cleared up.

[35] F. L. Mohler, Bur. Stand. Research Pap. 485, **9**, 494 (1932).

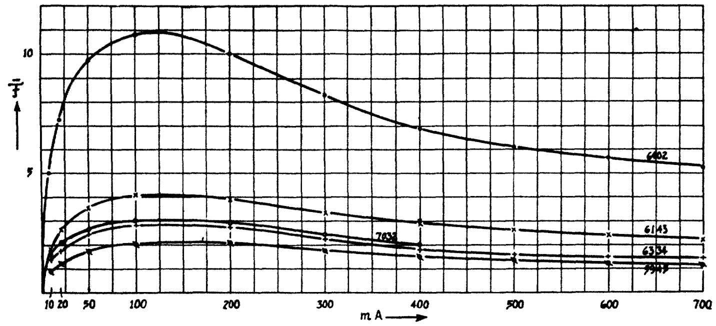

FIG. 7. Change of F values of s_5 lines with higher currents.

that the number of excited atoms approaches with increasing current the equilibrium values corresponding to a Boltzmann distribution of the electron temperature. Furthermore, he deduced a similar result for the positive column of mercury from the data of Killian.[36] It seems therefore that the connection between electron temperature and specific temperature and the approximation of a statistical equilibrium between electrons and excited atoms with increasing current is really a general property of monatomic gases as is to be expected from the general theoretical considerations presented above.

IV. INFLUENCE OF HIGHER CURRENTS UPON THE DISPERSION OF EXCITED GASES AND THE EFFECT OF NEGATIVE DISPERSION

If the current exciting and destroying the neon atoms is increased above 100 m.a., the simple Eq. (8) no longer holds. The quadratic terms of Eq. (7) come into play and, besides this, the population of the higher levels $p_1 \cdots p_{10}$ increases, so that the expression

$$1-Q_{kj} \equiv 1-N_k g_j / N_j g_k$$

in Eq. (1) for F cannot be neglected. Such experiments with very high currents which were carried out by Kopfermann and Ladenburg,[37] gave the first experimental evidence for the existence of the negative terms in the dispersion equation for the dispersion, i.e., for "negative dispersion" (see report of Korff and Breit,[1] p. 481).

The results of these measurements are given in Fig. 7 which contains the F values of different neon lines, having the lower level s_5 in common, up to currents of 700 m.a. For such high currents the rather narrow tubes (0.8 cm diameter) had to be made of quartz and cooled with running water. We see from Fig. 7 that the F values of the lines 6402 (s_5p_9), 6334 (s_5p_8), 6143 (s_5p_6), 5945 (s_5p_4) increase only slightly above 60 m.a. up to about 100 m.a. but with higher currents they definitely decrease. If the F values of the different lines are again reduced to the same scale, so that they agree for a small current (e.g., 10 m.a.) (see Fig. 8), these reduced values $\bar{F}$ coincide as was mentioned above within the limits of error up to 60 m.a. But with higher currents, especially above 100 m.a., the lines behave quite differently, the reduced F values no longer coincide, but separate considerably from one another. Those of longest wavelengths decrease most, and those of shorter wavelengths decrease least, i.e., the smaller the difference of energy between the common lower state s_5 and the different upper states p_k the larger is the decrease of F. This is just what we should expect as a consequence of negative dispersion and the influence of the expression Q_{kj} in the formula (1) (j corresponds in these experiments to s_5 and k to p_4, p_6, p_8 and p_9): the larger the current the greater is the number of the atoms in the upper state p_k; at the same time the atoms in the lower state s_5 do not increase

---

[36] Killian, Phys. Rev. **35**, 1238 (1930).

[37] Reference 9, VI, see also H. Kopfermann and R. Ladenburg, Zeits. f. physik. Chemie (A) Haberband, 378 (1928).

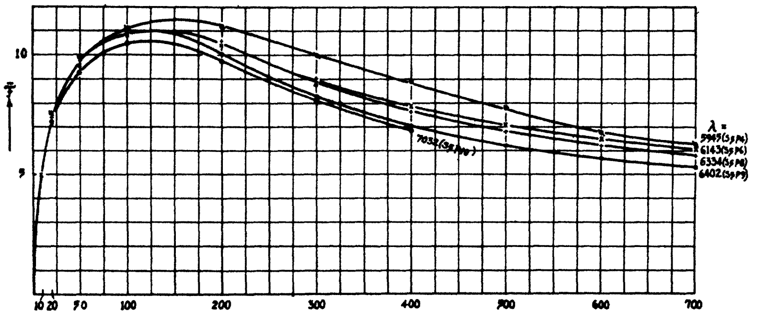

FIG. 8. F values of Fig. 7 reduced to the same scale.

much but rather decrease a little above 100 m.a. as a discussion of Eq. (8) shows (see the following section). Therefore with increasing current the ratio N_k/N_j increases. Furthermore the number N_k of atoms in the different upper states (i.e., $p_{10}\cdots p_2$) will be greater the lower the energy of that state and the higher its statistical value, as a consequence of a kind of statistical equilibrium as we shall see in Section V.

The main point is the difference of decrease between the $\bar{F}$ values of the different lines. This difference can *not* be explained by the decrease of the population of the s_5 level, for this is the same for the different lines. Neither does this difference come from a change of the A values which are different for the different lines, for the following observations[38] prove without doubt that the population of the higher levels p_4, p_6, p_8 and p_9 is increased by increasing current so much that the expression Q in Eq. (1) for F can no longer be neglected.

Firstly, absorption measurements of the line $p_{10}-s_1$ (7059) gave the result that the absorption becomes appreciable above 50 m.a. and increases with the current. Secondly, the "reversal temperature" of the neon lines, i.e., the black temperature of the light source at which the neon lines just disappear against the continuous background, was measured with a carbon arc as light source. This reversal temperature was lower than 4000° for a current of 50 m.a. and increased strongly with increasing current. According to the cited considerations of Hedwig Kohn[7] this means that the value Q for the lines in question is smaller than 0.01 for 50 m.a. but increases with higher currents. Thirdly, the increase of the intensity of the k–j lines above 50 m.a. showed that the number of N_k atoms increased further.

All these different experiments prove without doubt, that the population of the p levels does increase with the current, and so much so that above 100 m.a. the ratio Q has appreciable values. Therefore the experiments shown by the curves of Fig. 8 prove the influence of the negative term in the dispersion formula. This "negative dispersion" corresponds to the negative absorption of the theory of radiation and to the term -1 in the denominator of Planck's formula for the radiation of a black body (Eq. (5)), as is easily shown by Einstein's derivation of this formula. The influence of this term comes into play with radiation measurements only, if these are carried out at rather high temperatures or with long wave-lengths, as the classical experiments of Lummer-Pringsheim and Rubens-Kurlbaum[39] show. With these high temperatures and long wave-lengths the expression $h\nu/KT$ in the exponential of Planck's formula becomes so small that the -1 can no longer be neglected and in the limit Planck's formula goes over into Rayleigh's formula. In a similar way we find here the influence of negative dispersion only at very high currents, and this influence is the stronger

---

[38] Reference 9, V and VI.

[39] O. Lummer and E. Pringsheim, Verh. d. Deutsch. Physik. Ges. **2**, 163 (1900). H. Rubens and F. Kurlbaum, Berliner Akad. Ber. 929 (1900); Ann. d. Physik **4**, 649 (1901).

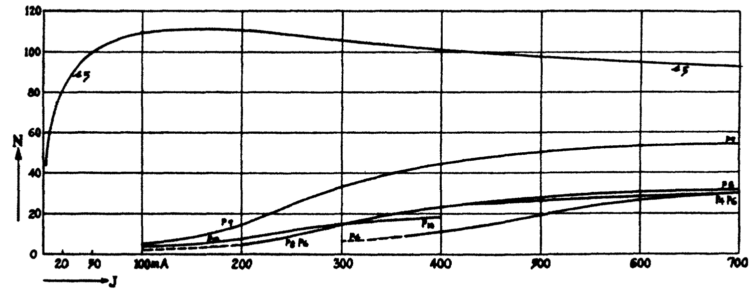

FIG. 9. Change of the population of s_5 and of different p levels with current (neon pressure 1 mm).

the smaller the energy difference of the two levels considered, i.e., the longer the wave-length at which the anomalous dispersion is investigated.

V. THE STATISTICAL EQUILIBRIUM BETWEEN THE s AND p STATES OF NEON

We are now ready to calculate from the cited experiments the relative number of the different excited s and p levels of neon. According to Eq. (1)

$$Q \equiv N_k g_j / N_j g_k = 1 - F_{kj} / N_j f_{kj}.$$

The values of F are given directly by the experiments, but the value of N_j and its change with the current are known only up to about 60 m.a. below which the linear relation (Eq. (8)) holds and the negative dispersion does not yet come into play. For higher currents an extrapolation of the change of the population of N_j with current is necessary. By using the quadratic Eq. (7) deduced by theoretical considerations of the exciting and destroying processes mentioned above, this Eq. (7) can be written in the somewhat simpler form

$$N_j = (\alpha I + \beta I^2)/(\gamma I + \delta I^2 + 1). \qquad (7a)$$

The discussion of the experiments on anomalous dispersion and their comparison with Eq. (7a) led to the following values[40] valid only under the experimental conditions.

$$\alpha = 7 \cdot 10^{10}, \quad \beta = 1 \cdot 10^8, \quad \gamma = 5 \cdot 10^{-2}, \quad \delta = 1.5 \cdot 10^{-4}.$$

Values of N_{s_5} so calculated are plotted in Fig. 9. As a matter of fact it will not make much difference in our conclusions if the N values decrease or increase a little above 100 m.a. Knowing the values of N_{s_5} we are able to calculate the ratios N_{p_k}/N_{s_5} from the experiments and we get the values N_p drawn in Fig. 9. This figure shows that below 100 m.a. the number of atoms in the p_k levels is very small compared with N_{s_5}; with increasing current the values of N_p increase, but very soon they approach saturation and statistical equilibrium. With 700 m.a. they are arranged nearly according to their energy and their statistical weight. If we put

$$Q_{kj} = \exp\left(-(E_k - E_j)/K\Theta\right),$$
$$\Theta = 0.621/\lambda_{kj}(-\log Q_{kj}),$$

where j corresponds to s_5, and k to the different p values, and where

$$E_k - E_j = hc/\lambda_{kj}, \quad hc/\log e = 0.621.$$

Θ, the specific temperature, is a measure of the ratio N_k/N_j. For the five s_5 lines we get the values shown in Table V. The differences between the Θ values for the different p values with $I = 700$ m.a. are within the limits of error and we may speak of a kind of statistical equilibrium

TABLE V. *Values of $Q(=N_k g_j/N_j g_k)$ and of Θ for different currents in neon.*

	..............Q_{kj}............			Θ
λ	$I = 300$ m.a.	500 m.a.	700 m.a.	For $I = 700$ m.a.
7032	0.23	—	(0.40)	22,000°
6402	0.21	0.37	0.43	26,500°
6334	0.14	0.29	0.38	23,400°
6143	0.15	0.27	0.35	22,200°
5945	0.16	0.20	0.33	22,700°

---

[40] Reference 9, V, p. 180.

between the p states, their common specific temperature being about 23,000°K. This is in satisfactory agreement with the value deduced in Section III for the specific temperature of the s states relative to the normal state and with the electron temperature as measured by Seeliger and Kirchert.[26]

We may summarize these results as follows: In the positive column called the "plasma" of pure neon, and more generally of monatomic gases, where the electrons possess a nearly Maxwellian distribution of velocities, a statistical equilibrium between electrons and excited atoms is approached with increasing current. The specific temperature determining the relative population of a definite excited level approaches the electron temperature, when de-excitation of the atoms is mainly produced by collisions of the second kind with electrons, i.e., when these collisions overbalance to a large extent the other destroying factors, such as collisions with the walls or other atoms and decay by spontaneous radiation. This "equilibrium current" is the higher, the higher the energy of the excited level. Therefore one gets only at very high currents a statistical equilibrium for different excited levels with the same specific temperature. The kinetic energy of the normal atoms does not participate in this equilibrium. Their real mean temperature is of a totally different order of magnitude.

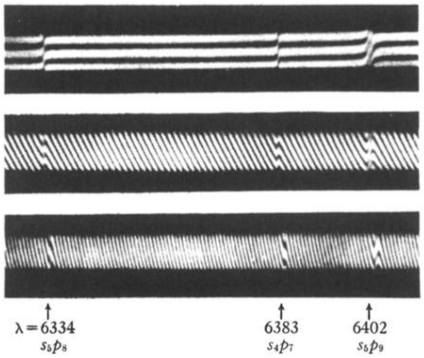

FIG. 2. Pictures of anomalous dispersion near some neon lines.