Spectroscopic Investigation of a Hydrogen and Helium Plasma in a P. I. G. Discharge

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(Z. Naturforschg. **20 a**, 184—192 [1965]; eingegangen am 2. Oktober 1964)

The intensities of spectral lines emitted from a low pressure P. I. G. discharge running in hydrogen and helium gas have been measured, and the population densities of the corresponding excited levels have been calculated from there. It was found that the population densities of the excited states do not follow the values given by the Saha equation. The probable reason for this deviation is the influx (or diffusion) of the neutral atoms into the plasma column. A model which takes into account the free diffusion of the surrounding gas atoms into the plasma column permits an explanation of the observed phenomena. Using this model and solving the corresponding rate equations, electron temperatures of several electronvolts have been obtained for both gases. These temperatures are confirmed by mass spectrometric abundance measurements of the He^{+}- and He^{2+}-ions, in conjunction with the coronal ionization formula.

The P.I.G. discharge (reflex arc) is not only a very useful device for measuring the pressure in vacuum systems, but serves in plasma physics as one of the possibilities for creating a highly ionized plasma. In our laboratory, a P.I.G. discharge has been developed [1] for the dissociations of molecular ions injected into a magnetic mirror machine (M.M.I.I.). In general, this P.I.G. discharge is fed by lithium vapour at densities of about $10^{13}\ \mathrm{cm}^{-3}$.

Spectroscopic measurements of the line intensities emitted from the Li-plasma led to electron temperatures which did not agree with the temperatures deduced from mass spectrometric abundance measurements and those obtained with a Langmuir probe. The spectroscopically obtained temperatures were 10 to 50 times lower than the temperatures derived by the other two methods.

Therefore, the P.I.G. discharge was run in hydrogen and helium gas. Applying the steady-state equations for a non-thermal plasma, we obtained the same low temperatures from the measured line intensities as in the case of the lithium discharge. A significant feature was that the logarithms of the measured population densities did not follow a straight line when plotted as function of the excitation energy.

The measured population densities for the lower excited states of hydrogen are similar in form to those measured in an electrodeless high frequency discharge [2]. The measured population densities of He I and He II as function of the excitation energy show about the same relative dependance as measured in a hollow cathode discharge [3]. To explain this "abnormal" behaviour of the measured population densities, in both publications (l. c. [2, 3]) it was assumed that the plasma contained at least two groups of electrons, a cold one and another one of high energy [4]. The low density component N_e with high temperature t_e is assumed to be responsable for ionization, and the group with high density n_e and low temperature T_e will then be responsable for recombination. Plotting the logarithms of the measured population densities as functions of the excitation energy, it has been found [2] that they approximately follow a straight line. The slope defined the temperature T_e. It was further found that the absolute and relative values of the recombination continuum followed the equation:

$$\varepsilon(\nu) = C \cdot \frac{n_+ \, n_e}{(k \, T_e)^{3/2}} \exp\left(-\frac{h(\nu-\nu_g)}{k \, T_e}\right),$$

and it was concluded that the population of the higher excited states is mainly due to radiative plus

[1] M. Fumelli, Rapport EUR-CEA-FC-155, April 1962.

[2] H. Schlüter, Z. Naturforschg. **16 a**, 972 [1961]; **18 a**, 439 [1963]. — See also C. R. Vidal, Z. Naturforschg. **19 a**, 947 [1964].

[3] J. G. Hirschberg, E. Hinnov, and F. W. Hofmann, Proc. 6th Int. Conf. Ionization Phenomena in Gases, Paris 1963, Editeur Serma, Paris 1964, Vol. III, p. 359.

[4] Groups of electrons with different energies have often been measured (see for instance [5–7]) and by their existence one can in principle explain the spectroscopically measured population densities.

[5] J. D. Swift, Proc. 5th Int. Conf. on Ionization Phenomena in Gases, Munich 1961, North-Holland Publishing Co., Amsterdam 1962, Vol. I, p. 343.

[6] R. G. Meyerand et al., Proc. 5th Int. Conf. on Ionization Phenomena in Gases, Munich 1961, North-Holland Publishing Co., Amsterdam 1962, Vol. I, p. 333.

[7] N. D. Twiddy, Proc. Roy. Soc., Lond. A **275**, 388 [1963].

three-body collisional recombination processes of *the cold electrons*. The measurements were carried out [l. c. [2, 3]] at total particle densities n_0 of about $1 \cdot 10^{15}$ to $5 \cdot 10^{15}$ cm^{-3}, the densities n_e and n_+ were of the order of 10^{12} to 10^{13} cm^{-3}.

In our experiment, the total particle densities were of the order of 10^{13} to 10^{14} cm^{-3}, and the electron densities were of the same order of magnitude. Although the intensities of H_α and H_β, for instance, were rather strong, the spectral lines originating from highly excited states with principal quantum numbers $i > 10$, and the recombination continua could not be evaluated, even for exposure-times of one hour and more. This indicates a rather high temperature for the main part of the electrons. Although the observed feature can also be explained – in our case – by different groups of electrons or by one group of electrons with a non-MAXWELLian distribution of energy we have omitted these two possibilities.

In this article it is shown that the assumption of different groups of electrons is not absolutely necessary, the spectroscopically measured population densities can also be explained by a single group of electrons with a MAXWELLian distribution of energy, if the diffusion of the neutral gas atoms into the plasma column is taken into account. Moreover, this electron group leads to an ion-electron production which is consistent with the condition of charge neutrality and the observed currents in the discharge.

The electron temperatures so obtained are of several electron volts, in rather good agreement with mass spectrometric abundance measurements for He^+ and He^{2+}.

Experimental

The apparatus used for our measurements is the same as described in [1]. Instead of lithium-vapour hydrogen and helium gas was employed. A schematic drawing of the experimental arrangement is shown in Fig. 1.

The arrangement of the electrodes is basically the same as used in a conventional P.I.G. discharge. The main discharge burns between the cylindrical hollow anode, A, where the gas is introduced, and the water-cooled cathode K_1. The water-cooled cathode K_2 acts as reflector for electrons. The anode is grounded together with the whole vacuum system, the latter being made from stainless steel. The same negative potential is applied to both cathodes. The confining magnetic field is in axial direction; it is produced by two coils C.

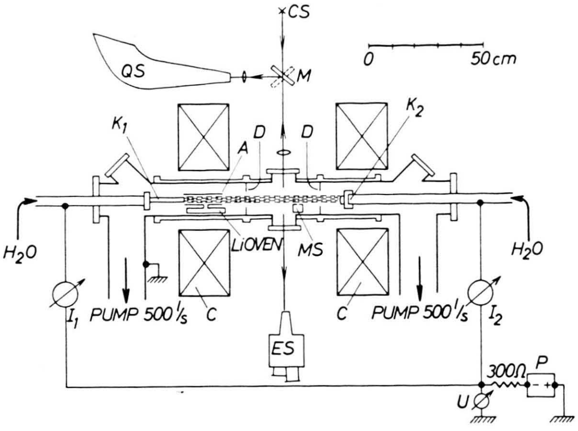

Fig. 1. Experimental arrangement (schematic drawing). A = hollow anode with inner diameter of $2\,R_0 = 3$ cm; K_1 = cathode 1; K_2 = cathode 2 (reflector); D = diaphragm; MS = mass spectrometer for abundance measurements or electrostatic probe; QS = HILGER medium quartz spectrograph; ES = REOSC echelle spectrograph; M = mirror; CS = calibration source; P = power supply; C = magnetic coil; the distance between K_1 and K_2 is $L = 65$ cm.

The field strength between the two coils is half as high as in the center of the coils.

When the discharge is running a plasma column of about constant brightness extends along the axis from cathode K_1 to cathode K_2. The diameter of this column is approximately equal to the inner diameter $2\,R_0$ of the hollow anode A, i. e. $2\,R_0 = 3$ cm. Typical parameters of the discharge are:

Hydrogen pressure	$p = 1 - 3 \cdot 10^{-3}$ mm Hg.
Helium pressure	$p = 5 \cdot 10^{-3} - 2 \cdot 10^{-2}$ mm Hg.
Current	$I_1 = 1 - 1.5$ amp.
Current	$I_2 = 0.2 - 0.5$ amp.
Applied voltage	$U = 400 - 600$ volt.
Magnetic field strength	$B_z = 1000 - 3000$ G.

The current I_2 is a pure ion current, since electrons are repelled by the cathode K_2. A mass spectrometer MS with its entrance slit at a radial distance of $r \cong 2$ cm served for abundance measurements of different ionic species.

For relative and absolute calibration of the photographic plates, we used the continuum emitted from the positive crater of a D. C. carbon arc. Quartz achromats served for observing both the discharge and the crater. All measurements were made in the center of the machine, observing the plasma column "side-on". The observed line intensities were converted into "radial" line intensities applying the ABEL integral equation. The numerical calculations were carried out on a special analogue computer [8].

The population densities $n_i/\tilde{\omega}_i$ have been deduced from the line intensities I_{ij} using the familiar formula

$$I_{ij}(r) = \int_\nu J_{ij}(\nu)\,\mathrm{d}\nu = \frac{\Omega\,\Delta t}{4\,\pi}\,A_{ij}\,h\,\nu_{ij}\,n_i(r) \qquad (1)$$

[8] L. BECKER and H. W. DRAWIN, Z. Instrumentenkde. 72, 251 [1964].

where Ω = angle of observation, Δt = exposure-time, A_{ij} = spontaneous transition probability, ν_{ij} = frequency, h = PLANCK's constant, $n_i(r)$ = number density of i^{th} state, at radial distance r.

Experimental Results
Application of Saha's Equation

The densities n_i thus obtained and then divided by the statistical weights $\tilde{\omega}_i$ have been plotted in a semi-logarithmic scale and are shown in Figs. 2 and 3 for two different radial distances r. It is a remarkable feature that the measured values do not lie on a straight line at high principal quantum numbers i. The values for H I and He I decrease very rapidly with increasing principal quantum number, whereas the He II shows a slight increase.

One would expect that all $\log(n_i/\tilde{\omega}_i)$ values should lie on a straight line at high principal quantum numbers i, since from the solution of the rate equations in the case of a steady-state plasma it is known [9–12] that for higher excited states SAHA's equation is always applicable in the form:

$$\frac{n_+ \, n_e}{n_{r,i}} = \frac{2 \, \Sigma_+}{\tilde{\omega}_{r,i}} \cdot \frac{(2 \pi m k T_e)^{3/2}}{h^3} \exp\left\{-\frac{\Delta E_i}{k T_e}\right\}. \quad (2)$$

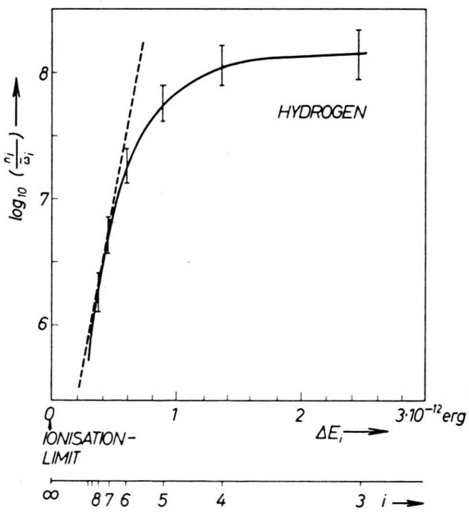

Fig. 2. Measured population densities for hydrogen, at r=0.25 cm.

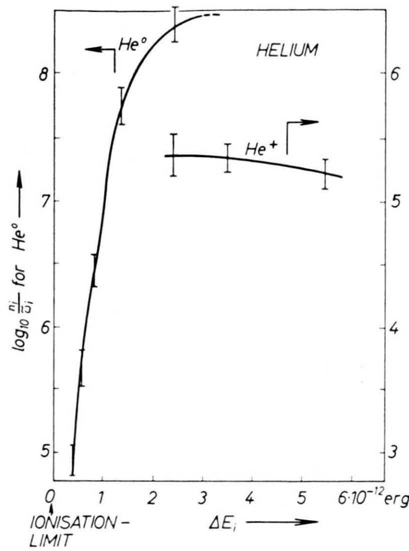

Fig. 3. Measured population densities for helium, at r=0 cm.

If SAHA's equation is valid one should be able to derive the electron temperature T_e from the slope of a straight line given by the $\log(n_i/\tilde{\omega}_{r,i}) - \Delta E_i$-curve at high principal quantum numbers i. Although in our case a straight line is not well defined by the measured curves in Figs. 2 and 3, we can nevertheless try to derive T_e from the slope of a *tangent* which we put at large values i (i = 6 to 8) on the measured curves. The temperatures derived from this slope can now be used for calculating the electron density n_e (= ion density n_+) from equation (2). (For n_i one has to take a value at high principal quantum numbers). The values for T_e and n_e obtained by this method are shown in Fig. 4 and Fig. 5. Especially the temperature values are extremely low.

The temperature values obtained are in complete disagreement with those derived from mass spectrometric abundance measurements [13]. From mass spectrometrically measured ratios of the ion currents I(He^+) and I(He^{2+}) – with the He^+-peak corrected for H_2^+ ions – one derives from the coronal ionization formula an electron temperature at $r \cong 2$ cm of about [14]

$$k T_e \cong 6 \ldots 7 \text{ eV}.$$

[9] R. W. P. McWHIRTER, Nature, Lond. **190**, 902 [1961].
[10] R. W. P. McWHIRTER and A. G. HEARN, Proc. Phys. Soc., Lond. **82**, 641 [1963].
[11] H. W. DRAWIN, Ann. Phys., Lpz. **14**, 262 [1964].
[12] H. W. DRAWIN, Z. Naturforschg. **19 a**, 1451 [1964].
[13] The non-observed recombination continua sets also a lower limit for the electron temperature, and this temperature is also in disagreement with the temperatures of Figs. 4 and 5.
[14] We note that probe measurements made on the Li-discharge indicated a temperature of 8–9 eV, whereas from the ratio of the Li^+- to Li^{2+}-ion currents in the mass spectrometer a temperature of 8 eV was obtained [15].
[15] H. W. DRAWIN and M. FUMELLI (to be publ.) – See also Rep. EUR-CEA-FC-270-Fontenay-aux-Roses 1964.

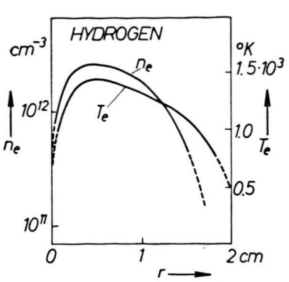

Fig. 4. Electron density n_e and temperature T_e obtained from SAHA's equation, as function of radius r. $B_z = 2966$ G, $p \cong 2\cdot10^{-3}$ mm Hg.

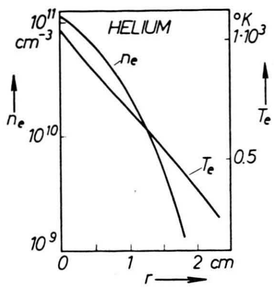

Fig. 5. Electron density n_e and temperature T_e obtained from SAHA's equation, as function of radius r. $B_z = 1180$ G, $p \cong 2\cdot10^{-2}$ mm Hg.

Moreover, the temperatures in Figs. 4 and 5 are not possible for a (self)sustaining discharge in a steady state. For a steady-state discharge with $n_e \cong 10^{12}$ cm^{-3} at total particle densities of $n \cong 10^{13}$ cm^{-3} one needs at least a temperature of 1.4 eV [10–12].

Such low temperatures are possible only in a decaying plasma. But as has already been shown earlier [3, 16–18] the population densities of decaying plasmas follow at high values i a straight line, which is not the case here. Therefore, the spectroscopically derived temperatures and electron densities of Figs. 4 and 5 must be wrong. The discrepancy immediately can be solved by the assumption of different groups of electrons, as done by different authors (l. c. [2, 3]). But the reason for the mentioned discrepancy may also be due to another fact, namely the large mean free paths Λ_0 of the particles at low particle densities. At neutral particle densities, $n_0 \leqq 10^{13}$ cm^{-3}, Λ_0 can be of the same order of magnitude or even larger than the diameter $2\,R_0$ of the discharge column. The particles can traverse the column with their thermal velocities v_t ($v_t \cong 10^5$ to 10^6 cm sec^{-1}) without being completely ionized. Although a steady-state is established, the plasma column will not be in equilibrium with the surrounding gas as for as the excitation, ionization, and recombination processes are concerned. Therefore, the steady-state equations are not applicable in their usual form, and further, equation (2) will not be valid.

To calculate the population densities of the excited states we will replace the usual "static" model by a "dynamic" model in which the large mean free paths Λ_0 of especially the neutral particles are taken into account.

Theoretical

We assume a cylindrical plasma column imbedded in a neutral gas atmosphere (Fig. 6). The pressure p_0 is so low [19] that $\Lambda_0 \geqq R_0$ is valid. We assume that the neutral particles have had their last collision

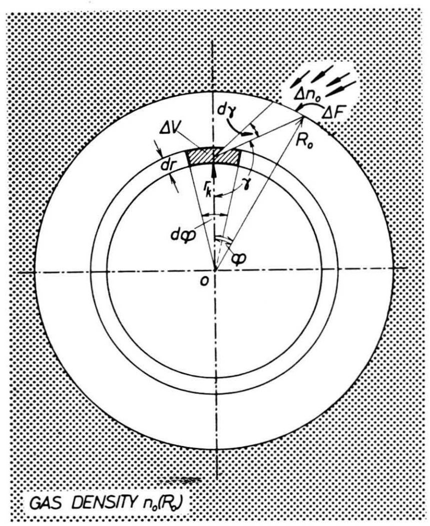

Fig. 6. Model of a plasma column. At R_0 the density of neutral atoms is n_0. The number density Δn_0 diffuses through the surface ΔF into the volume element $\Delta V(r_k)$. Integration over γ and r yields equ. (3), when ionization and recombination between R_0 and r_k is taken into account.

with another neutral particle or ion at the edge of the plasma column. The column may have a radial temperature distribution $T_e(r)$ and an electron density distribution $n_e(r)$. Neutral particles may enter continously from all the sides into the column

[16] R. W. MOTLEY and F. KUCKES, Proc. 5th Int. Conf. on Ionization Phenomena in Gases, Munich 1961, North-Holland Publishing Co., Amsterdam 1962, Vol. I, p. 651.

[17] E. HINNOV and J. G. HIRSCHBERG, Phys. Rev. **125**, 795 [1962].

[18] F. ROBBEN, W. B. KUNKEL, and L. TALBOT, Phys. Rev. **132**, 2363 [1963].

[19] For a pressure of $p_0 = 1\cdot10^{-3}$ mm Hg one has for hydrogen $\Lambda_0 = 8.8$ cm, for helium $\Lambda_0 = 13.3$ cm, for argon $\Lambda_0 = 4.7$ cm.

and leave it on the opposite side. Only some of them will suffer collisions with electrons with a collision frequency depending on the electron temperature and the electron density.

From the two-dimensional model Fig. 6 one can calculate the number density $n_0(r_k)$ of particles n_0 at a fixed radial distance $r=r_k$. One obtains from a simple geometrical consideration the formula

$$n_0(r_k) \cong n_0(R_0)\,\frac{1}{\pi}\int\limits_{\gamma=0}^{\gamma=\pi}\left[\exp\left(-\int\limits_{r=r_k}^{R_0} n_e(r)\,\frac{S(r)-Q(r)}{v_t}\cdot\frac{r\,dr}{(r^2-r_k^2\sin^2\gamma)^{1/2}}\right)\right]d\gamma \tag{3}$$

where $n_0(R_0)$ = number density at the edge of the plasma column at $r=R_0$, v_t = mean thermal velocity of neutral gas atoms, $S(r)$ = ionization (or dissociation) coefficient, $Q(r)$ = recombination coefficient (radiative plus collisional recombination).

A special simplification of equation (3) may be mentioned: With a temperature so high that $Q(r) \ll S(r)$, and with the rectangular distributions

$n_e = \text{const}$ for $0<r<R_0$; $n_e=0$ for $r>R_0$; $T_e=\text{const}$ for $0<r<R_0$; $T_e=0$ for $r>R_0$

equation (3) reduces to

$$n_0(r_k) = n_0(R_0)\,\frac{1}{\pi}\int\limits_{\gamma=0}^{\gamma=\pi}\left[\exp\left(-\beta\left\{\left[1-\left(\frac{r_k}{R_0}\right)^2\sin^2\gamma\right]^{1/2}-\frac{r_k}{R_0}\cos\gamma\right\}\right)\right]d\gamma \tag{4}$$

where $\beta = \frac{n_e S}{v_t} R_0$, $S = \int\limits_{v_i}^{\infty} v_e\,\sigma\,f(v_e)\,dv_e$, $f(v_e)$ = velocity distribution of electrons.

Especially for $r_k=0$ one obtains from equation (4) the familiar formula

$$n_0(0) = n_0(R_0)\,e^{-\beta}, \tag{5}$$

and for $r_k=R_0$ (integrating from $-\pi/2$ to $+\pi/2$)

$$n_0(r_k=R_0) = n_0(R_0)\,.$$

To obtain now the population densities $n_i/\tilde{\omega}_i$ for a radial distance r_k one has to solve the corresponding rate equations

$$\frac{dn_i}{dt} = \sum_{i\neq j} K_{ij}^{(+)} - \sum_{i\neq j} K_{ij}^{(-)} - \nabla\Gamma_i \tag{6}$$

for a stationary state *with a total particle density* n_0 *imposed by equation (3) or equation (4).* $K_{ij}^{(+)}$ and $K_{ij}^{(-)}$ denote the rate coefficients for populating and depopulating the level i. $\nabla\Gamma_i$ is a diffusion term. For the steady state the condition is

$$dn_i/dt = 0; \quad i=(1),2,3,\dots,p. \tag{7}$$

Further we pose $\nabla\Gamma_i = 0$.

Equation (7) has been solved for H, He I, and He II, with the assuption of a MAXWELLian distribution of energy for the electrons [20]. We have found that the population densities can be represented by a simple formula if the condition $n_e < n_0$, n_r is fulfilled. Then it follows

$$\frac{n_{r,i}}{\tilde{\omega}_{r,i}} \cong n_r\,n_e\,\frac{P_{r,i}(n_e,T_e)}{\tilde{\omega}_{r,i}} = n_r\,n_e\,P'_{r,i}(n_e,T_e)\,. \tag{8}$$

The index r denotes the stage of ionization (e. g. $r=0$ for neutral particles, etc....) and $P'_{r,i}(n_e,T_e)$ is a complicated function of n_e, T_e, the transition probabilities, the oscillator strengths, etc.

Some typical results of our numerical calculations are shown in graphical form in Figs. 7 to 14. Before drawing the curves, the $P'_{r,i}$ have been multiplied by the arbitrary factors 10^{22} for H I, 10^{23} for He I, and 10^{23}, 10^{24} or 10^{25} for He II. The following statistical weights $\tilde{\omega}_{r,i}$ have been used:

$$\tilde{\omega}_{0,i} = 2\,i^2 \text{ for H I},$$
$$\tilde{\omega}_{0,i} = i^2 \text{ for He I},$$
$$\tilde{\omega}_{1,i} = 2\,i^2 \text{ for He II}.$$

The relative behaviour of the calculated curves is obviously the same as that of the measured ones. This behaviour depends only on the electron density

[20] Assumption was made that the plasma is optically thin in all transitions. Also photo-ionization has been neglected. This is allowed for low particle densities. The calculations have been carried out on a small mechanical computer. A comprehensive electronic computer programme is in preparation. These calculations will give more exact values, and especially the behaviour of the population densities at very high principal quantum numbers will be seen.

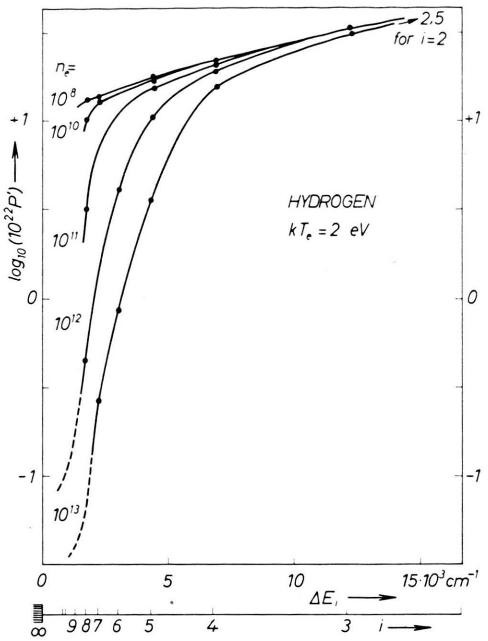

Fig. 7.

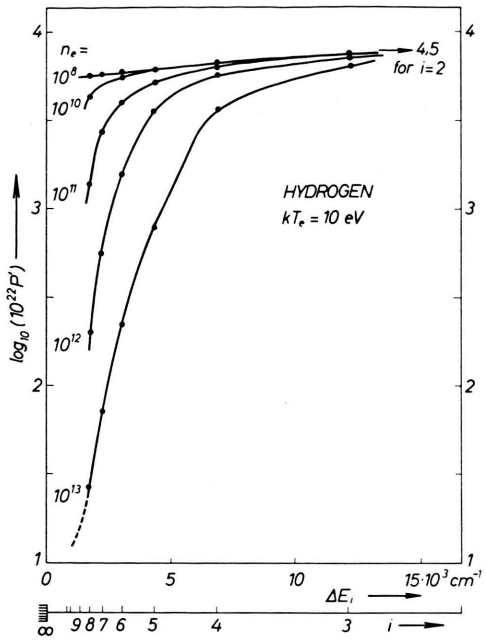

Fig. 8.

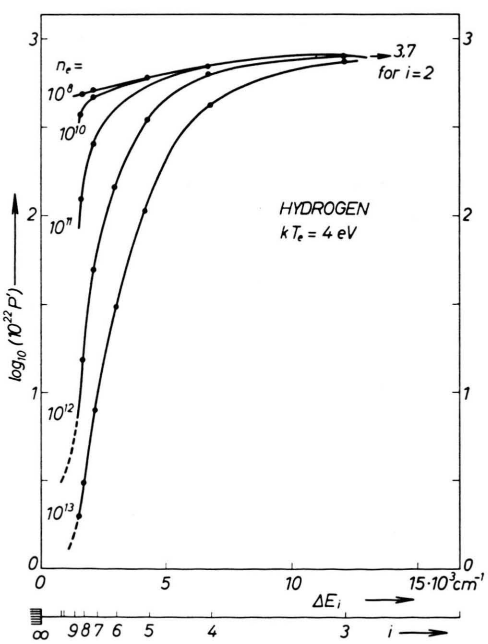

Fig. 9.

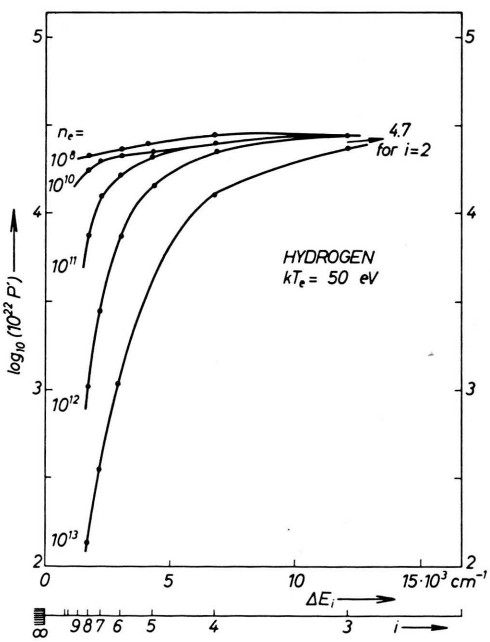

Fig. 10.

Fig. 7 to 10. The factor $P'(n_e, T_e)$ for hydrogen.

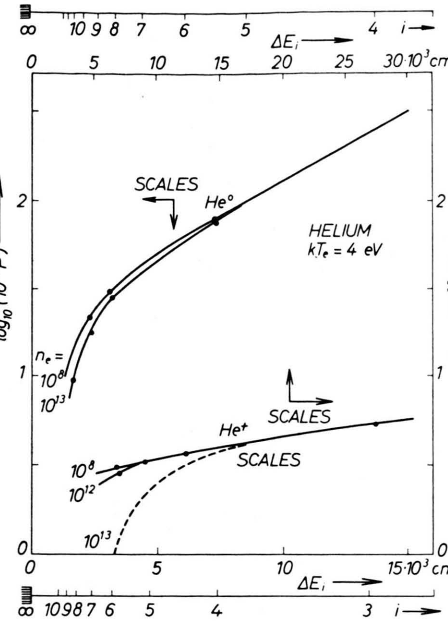

Fig. 11.

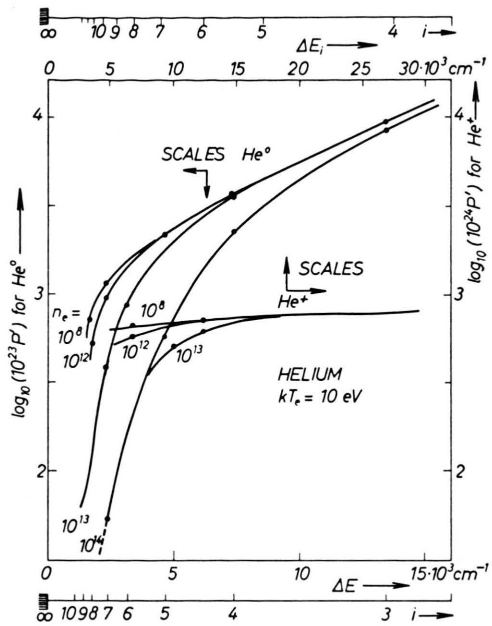

Fig. 12.

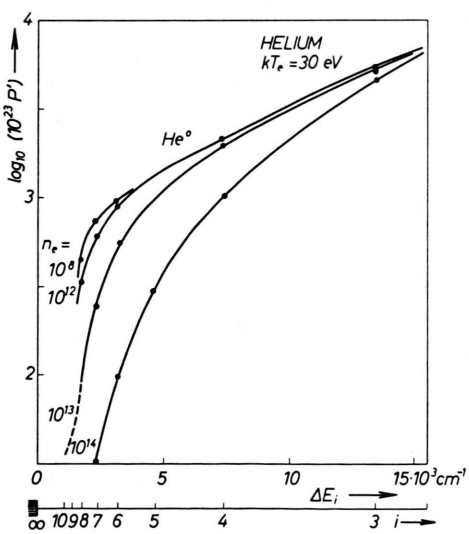

Fig. 13.

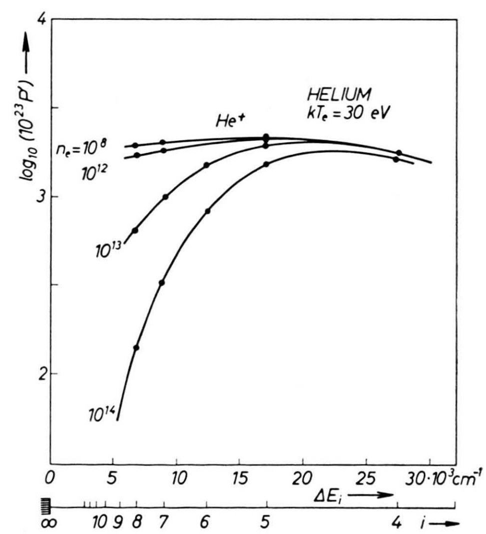

Fig. 14.

Fig. 11 to 14. The factor $P'(n_e, T_e)$ for helium.

n_e and on one single electron temperature T_e; the introduction of several temperatures is not necessary. It seems that the model used for our calculation can describe the observed phenomena in an adequate manner.

Comparing now the relative and the absolute values of the measured population densities with the calculated curves, one is able to derive n_e and T_e when n_0 is known. n_0 has been obtained from a pressure measurement [20a]. The observed population

[20a] An ionization gauge served for the pressure measurements. The indication of this type of gauge is directly proportional to n_0.

densities in the discharges are consistent with the following values for n_e and T_e:

Hydrogen	*Helium*
$n_0 \cong 3\cdot 10^{13}$ cm^{-3}	$n_0 \cong 4\cdot 10^{14}$ cm^{-3}
$n_e \cong 1$ to $3\cdot 10^{12}$ cm^{-3}	$n_e \cong 2.5\cdot 10^{13}$ cm^{-3}
$k\,T_e = 8$ to 11 eV	$k\,T_e = 11$ to 15 eV

These electron temperatures are much higher as one would expect; nevertheless, they are in agreement with the temperatures derived from the coronal ionization formula, using mass spectrometric abundance measurements of He^+ and He^{2+}. Concerning the ionization-recombination equilibrium between helium ions and electrons one is allowed to apply this ionization formula for densities $n_e < 10^{12}$ cm^{-3}, $n_+ < 10^{12}$ cm^{-3}, if $k\,T_e \geqq 1.5$ eV. In this case collisional processes from and into upper excited states are negligibly small. The He-ions are in a "quasi-steady state" with respect to the electrons, since electric and magnetic fields prevent them for leaving the plasma column directly, or with other words, the mean free paths or diffusion lenghts of the ions are much smaller than the diameter of the plasma column.

A measurement of the ratio of the ion currents, $I(He^{2+})/I(He^+)$, gives directly the ratio of the particle densities, since $I(He^{2+})/I(He^+)$ is about equal to $\frac{1}{2}\,n(He^{2+})/n(He^+)$. From the coronal ionization formula

$$n(He^{2+})/n(He^+) = S(T_e)/Q(T_e) \qquad (9)$$

(which does not depend on n_e) one calculates directly a (Maxwellian) temperature. This temperature will probably be slightly lower than the real temperature since also the He^+-ions are not in a completely steady state.

The high electron temperatures obtained cause a production rate of ion-electron pairs which is in good agreement with the measured currents. Using equation (3), the total number of ion-electron pairs, $Z_{\mp}$, produced per unit time in the whole plasma column of length L is given by the formula

$$Z_{\mp} \cong 2\,\pi\,L\,v_t \int_{r_k=0}^{R_0} r_k\,\{n_0(R_0) - n_0(r_k)\}\,\mathrm{d}r_k\,. \qquad (10)$$

With $n_e = 3\cdot 10^{12} = \text{const}$; $k\,T_e = 8\text{ eV} = \text{const}$; $v_t = 3\cdot 10^5$ cm/sec; $n_0 = 3\cdot 10^{13}$ cm^{-3}; $L = 65$ cm; $R_0 = 1$ cm one obtains for hydrogen $Z_{\mp} \cong 6\cdot 10^{18}$ sec^{-1}.

Multiplication with e yields a charge production which will be equivalent to a current of 0.9 amp. This is in reasonable agreement with the measured current $I_2 \cong 0.5$ amp. on the cathode K_2.

Conclusion

The temperature determination of a stationary low pressure discharge by spectroscopic means yields much too low values if the diffusion of the surrounding gas into the plasma column is not taken into account. The continuous influx of neutral gas into the column causes a considerable perturbation of the rate coefficients with respect to the usual case of a "static" steady-state plasma with no radial density and temperature gradients. Solving the steady-state equations with a neutral particle density given by the free influx of the particles into the plasma column, one will obtain population densities of the excited states which deviate considerably from those calculated by the steady-state equations without particle influx. The Saha-equation, in general applicable for the higher excited states, will no longer be valid, for either the lower, or for the upper excited states, if the particle influx becomes important. It is shown that both the electron temperature and the electron density can be obtained from spectroscopically measured population densities, if the particle influx is taken into account. It is an important feature that the observed population densities can be explained by a model using only one group of electrons with a well-defined temperature.

We note that the observed effect is already known in high pressure discharges for which thermal equilibrium can always be assumed. In these discharges the spectroscopically derived temperature *on the axis* can be some percent too low if the "equilibrium lengths" are larger than a certain amount of the "diffusion lenghts" in this region caused by the radial temperature distribution. In general, this effect is so small that it can be neglected. But this is not the case if we deal with non-thermal low pressure discharges, for which the free diffusion lengths are often much larger than the diameter of the whole plasma column. *The spectroscopically derived temperatures may therefore be incorrect if the diffusion is not taken into account.*

Concerning the calculation of the population densities, the following important remarks may be added:

1. The solution of equation (6) together with equation (3) or equation (4) can be regarded as the first approximation of a more complex problem in which the whole history of each single excited and non-excited atom during its travel through the plasma column is taken into account. This is specially important in those cases where the mean life-time of the excited states is larger than the time necessary for traversing the column.

2. If neutral particles – which enter from outside into the plasma column – undergo charge exchange collisions [21], equation (3) must be replaced by two similar equations, one taking into account that part of the atoms which traverse the plasma column without charge exchange collision, and another one which takes into account direction and velocity v_{ex} of the neutral traversing the plasma column after charge exchange collisions. If charge exchange collisions are so abundant that practically all neutral atoms will undergo these collisions, v_t in equation (3) may be replaced by v_{ex}, as a first approximation.

3. If the mean free paths Λ_0 of the atoms become smaller than the diameter of the plasma column, the described method for the determination of the population densities is no longer valid. With increasing pressure and/or increasing diameter of the plasma column, the population densities will approache those given by equation (6). But if strong radial temperature or density gradients are present equation (6) will once more be violated.

4. Dissociative recombination processes may play an important role in the transition region between the hot zone of the plasma column and the edge at R_0, and spectroscopically determined temperatures may be too high for this region. It is further known that H_2^+-, He_2^+-, Xe_2^+- etc. ions have rather large mobilities, and also their diffusion should be taken into account.

5. One should assume that at very high principal quantum numbers the logarithms of the population densities should follow a straight line of which the slope defines the temperature T_e. A continuous transition to the recombination continuum with the same temperature T_e should be assumed.

Acknowledgements

We wish to thank Prof. L. HERMAN and Dr. J. G. HIRSCHBERG for interesting discussions. The technical assistance of Mr. SABLON and Mr. ROUQUETTE during the measurements may gratefully be mentioned.

[21] This has been observed in the discharge running in hydrogen gas [22].

[22] H. W. DRAWIN and M. FUMELLI, Proc. Phys. Soc., Lond. (to be publ.).