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MEASUREMENT OF DISSOCIATION IN A HYDROGEN GLOW DISCHARGE*

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Abstract: Refractivity index measurements of the gas combined with manometric data and information on the energy dissipation in the positive column are utilized for the determination of the degree of dissociation in hydrogen glow discharge. The absence of perceptible distortion of interference frigges confirmes the basic assumption of the proposed method, that the radial density gradient is small and consequently the transfer of heat to the walls rather fast. The accuracy of the method is estimated to be better than ± 10%.

1. Introduction

Knowledge of the concentration of hydrogen atoms appeared indispensable in our investigation of the stationary striated positive column in hydrogen discharges. Thus far several methods for determining the degree of dissociation of molecular gases have been proposed[1, 2, 3], but only the Wrede's diffusion gauge[4] and the manometric method[5] have found more application. Both methods, however, require assumptions concerning the temperature of the molecular gas.

Here we describe a method for determining the degree of dissociation of hydrogen based on interferometric and manometric measurements combined with data on the power input in the positive column.

2. Theory

The gas under consideration, at an initial pressure p_1 and ambient temperature T_1 occupies the discharge tube of volume V_1 and an auxiliary recipient

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of volume V_2, communicating with the discharge tube. When the discharge is switched on, a fraction x of molecules is dissociated in the discharge and the gas temperature raised to T_2. Owing to both effects, a fraction f of molecules is pressed from V_1 into the side enclosure and the pressure in the system increases to p_2. If $V_2 > V_1$ the gas temperature in V_2 will little change; if, furthermore, the gas displaced from V_1 into V_2 consists only of molecules, or what is equivalent, if the atoms in V_2 quickly recombine one can write

$$(N_2 V_2 + f N_1 V_1)/V_2 = \frac{p_2}{k T_1}, \tag{1}$$

where f is related to the interferometric measurements of density in the discharge tube by

$$f = K \cdot \Delta s. \tag{2}$$

Δs denotes the number of displaced interference fringes, suitably expressed by the angle of rotation of the Jamin compensation plate; K is a constant of proportionality, depending on the length of the gas cells and the refractivity of the gas at a given wavelength; N_1, N_2 and k have their usual meaning.

Because of disturbing thermal effects, the measurment of f can be performed only shortly after switching on the discharge and the establishment of a stationary value of x. It is thus necessary to determine the value of T_2 attained at an instant t after the onset of the discharge.

The material balance equation for the system is given by

$$N_1 V_1 + N_1 V_2 = N_1 V_1 (1 - f)(1 - x) + 2 x N_1 V_1 (1 - f) + N_2 V_2, \tag{3}$$

where

$$N_1 (1 - f)(1 + x) = \frac{p_2}{k T_2}.$$

Taking into account that practically all energy dissipated in the positive column of a glow discharge is transferred to the walls and that there is no perceptible radial temperature gradient in the discharge tube (see below), one obtains T_2 by calculating the temperature of the inner surface of the discharge tube, T_s.

According to the well-known relation for transient heat flow through a semi-infinite medium, the energy W transferred to the wall is given by

$$W = \frac{x A \cdot (T_s - T_1)}{\sqrt{\pi \alpha t}}, \tag{5}$$

where $\varkappa$ is the coefficient of heat conductivity, A is the inner surface area, α is given by $\varkappa/(c_p \rho)$ with c_p the specific heat and ρ the density of the wall material.

Since $T_2 \sim T_s$ and $W = i \cdot X$, where X is the field and i the strength of the current flowing through the discharge tube, one obtains from Equs. (4) and (5) the degree of dissociation in the form

$$x = \frac{A \cdot p_2 \cdot \sqrt{\varkappa \rho c_p}}{k \cdot N_1 (1-f)\left[A T_1 \sqrt{\varkappa \rho c_p} + i X (\pi l)^{1/2} \right]} - 1. \tag{6}$$

This equation will be valid for other molecular gases too, provided the rate of heat transfer to the walls is sufficiently high.

3. *Apparatus*

A discharge and a reference tube, both of 100 cm length and $\varnothing_{in} = 9.5$ mm, were placed in a Rayleigh-Jeans interferometer and connected with a suitable vacuum and gas filling system (Fig. 1).

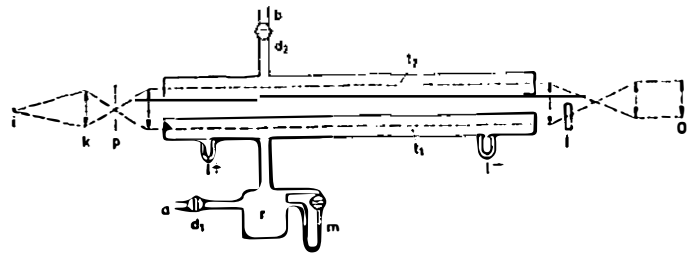

Fig. 1. Experimental arrangement: »*i*« — the pointolit source, »*k*« — condensing lens, »*p*« — inlet slit of the interferometer, »*j*« — Jamin compensating plate, »*o*« — auxiliary eyepiece, »t_1« — discharge tube, »t_2« — reference tube, »*r*« — side enclosure, »*m*« — differential manometer, »d_1« and »d_2« — glass valves allowing the isolation of »*r*« and »t_1« respectively »t_2«.

The discharge tube is fed from a 20 kV rectifier through a set of resistances. The reference tube is filled to the initial pressure »p_1« and afterwards separated from the discharge tube by means of the valve »d_2«. The pressure in the discharge tube and reference tube is measured by a calibrated LKB-gauge and the pressure increase in »t_1« and »*r*«, after separation from »t_2«, by the differential manometer m.

The entrance slit of the interferometer was illuminated by a 100 W — pointolit lamp, and in that way the brightness of fringes largely exceeded the luminosity of the discharge. The shift of the interference fringes was measured with respect to the cross hair of an auxiliary eyepiece »o«, as reference. In order to exclude any influence of the dilatation of the discharge tube upon the fringe shift, individual measurements were accomplished within time intervals ≤ 1 s after the onset of the discharge.

4. Results and discussion

Taking into account the limit of accuracy of the Zeiss interferometer and the absence of any perceptible distortion of interference fringes in the observed range of pressure and current strength, it can be concluded that radial

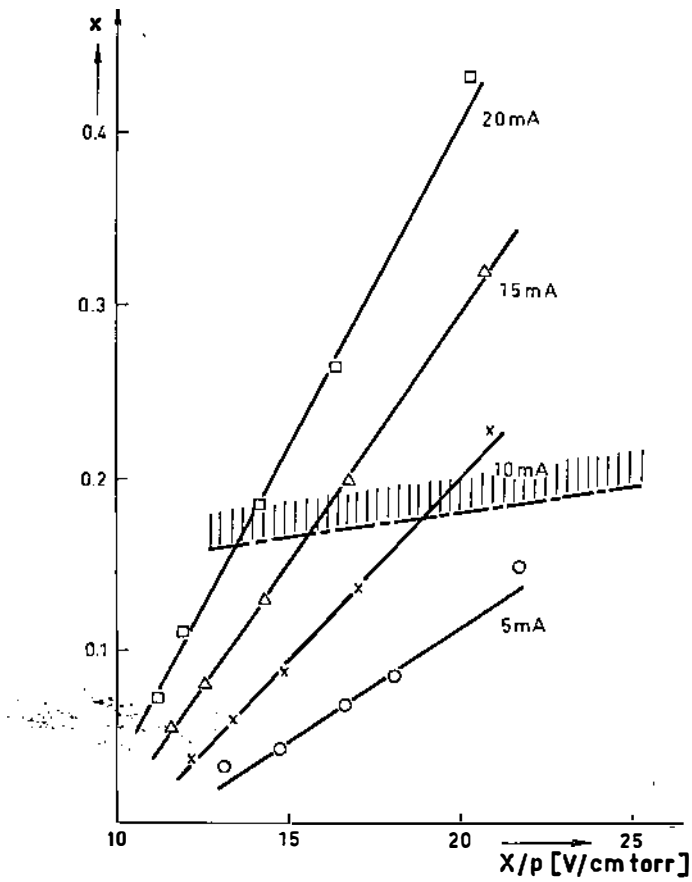

Fig. 2. A plot of degree of dissociation x vs reduced field strength X/p, with current strength as parameter. The dashed line denotes the limit above which standing striations are present in the positive column.

temperature gradient in the discharge tube was certainly smaller than 4 °K/cm at 4.5 torr or 12 °K/cm at 1.5 torr. Furthermore, the thermal boundary layer at the walls was found to be thinner than 0.33 cm, i.e., of the order of the mean free paths. Thus the maximum error introduced by the assumption $T_2 = T_s$ was $\leq 5\%$.

Fig. 2 shows the degree of dissociation as a function of the reduced field strength X/p. Each point represents an average of several measurements, and the accuracy is estimated to be better than 10%, including the error which might originate from the departure of T_2 from T_s. As expected, the plot x versus X/p is similar to the behaviour of the first Townsend coefficient, at first increasing almost linearly with the reduced field strength.

In the preceding consideration it was implicitly assumed that a Maxwellian energy distribution of atoms and molecules was established in the discharge. However, this does not strictly apply in the present case. Spectroscopic measurements of the Balmer line profiles showed that a small fraction of H-atoms was out of thermal equilibrium. This effect is most probably due to the formation of the antibound $1^3\Sigma_u$ H_2 molecules which dissociate into fast H-atoms of 2.2 eV kinetic energy. The contribution of the recently discussed mechanism[6] of acceleration of protons in the space charge zone, followed by neutralization at the surface, is of minor importance because of low ion densities and current strength in the positive column.

Although the interaction of atomic hydrogen with glass is rather complex and not yet sufficiently understood[7], the only slight departure from thermal equilibrium may be considered as a proof that the energy transfer of H-atoms to the walls proceeds at a rather high rate.

Furthermore, H-atoms with energies exceeding 0.3 eV enter with large probabilities in the metathetic reaction $H + H_2 \rightarrow H_2 + H$[3], thus transferring efficiently momentum to the H_2 molecules. Afterwards hydrogen molecules lose quickly their excess energy in collisions with the glass surface, for the accommodation coefficient of H_2 on glass is about 0.3[8]. In the present geometry the time interval between two consecutive collisions with the walls, $\tau \simeq 4\,r^2/D$, is estimated to be about $3 \cdot 10^{-4}$ s, and therefore the relaxation time is about 10^{-2} s.

It follows from the above discussion that the error arising from the basic assumptions used is small, and one may thus obtain reliable information on the degree of dissociation of hydrogen by Equ. (6) and the simple manometric method.

A fuller interpretation of the results shown in the Fig. 2 is not at present possible, since it requires data on the population of excited species and on the electron distribution function. Further work on the striated column is in progress.

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MJERENJE STUPNJA DISOCIJACIJE U TINJAVOM IZBIJANJU U VODIKU

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Sadržaj

Stupanj disocijacije vodika u tinjavom izbijanju je određen na osnovi mjerenja indeksa loma plina, tlaka i disipacije energije u pozitivnom stupu. Odsustvo zamjetljive distorzije interferentnih pruga potvrdilo je osnovnu pretpostavku metode da je radijalni gradijent gustoće slobodnih i vezanih H-atoma u izboju malen i da je prema tome prijenos topline na stjenke brz proces. Procjene pokazuju da je točnost metode bolja od ± 10%.