COMPARISON OF THE DECAY RATES OF PLASMA IN HYDROGEN AND DEUTERIUM

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The deionization rate in hydrogen and deuterium at pressures p = 15 to 600 μ Hg, tube diameters d = 3.2 to 6.5 cm and values of the preceding current I_0 = 60 to 1500 ma was studied by means of oscillographic observation of the ion current in a negative probe. Under the conditions employed the relative deionization rate in H and D decreased with time. The dependence of the rate of the process on the pressure is a non-monotonic function and goes through a maximum at pd $\sim 10^{-1}$ to 1 mm Hg·cm. The ratio of the deionization "time constants" (initial as well as final) in deuterium and hydrogen, τ_D/τ_H, is close to 1.4, i.e., $\approx (m_D/m_H)^{1/2}$ at all pressures both in the diffusion regime ($p < p_m$), and also in the recombination mode ($p > p_m$). The latter indicates that volume recombination under these conditions takes place primarily by means of triple collisions with neutral molecules ($M^+ + e + M$).

1. STATEMENT OF THE PROBLEM

IN decaying plasmas in different gases the rates of their deionization, all other conditions being the same (equal degrees of rarefaction and ionization, the same configurations of boundary surfaces, etc.), depend on a number of properties of the molecules of these gases: effective cross sections, masses, ionization and excitation potentials. In different isotopes of the same element the relative rates of deionization $\left(-\frac{1}{n}\frac{dn}{dt}\right)$ may differ only as a result of the difference in their atomic weights A. Different elementary processes in a gas are affected by the atomic weight in a different manner. Therefore, by means of studying the dependence of the rate of deionization upon A, we can judge as to which elementary processes play the main role in the deionization of the gas under given conditions. The object of our work was (1) to compare the rates of deionization of the hydrogen isotopes H and D (which have the most pronounced difference of atomic weights of all the stable gaseous isotopes), and (2) to compare their ratio with the ratio of the atomic weights of the two gases and to deduce from such a comparison possible conclusions with respect to processes that lead to the deionization of the gas.

2. METHOD AND APPARATUS

We measured the rate of deionization of the plasma that remains after the passage of $\frac{1}{4}$ cycle of 50 cps sinusoidal current, interrupted at the maximum. The investigation was carried out by oscillographic observation of the ion current in a negative probe introduced into the plasma. This method, used in a number of investigations,[1-3] enables us to observe deionization, i.e., the decrease in the concentration of positive ions, while high-frequency methods (references 4, 5, and others) indicate the rate of de-electronization, i.e., the decrease in concentration of free electrons.

An analysis of the conditions under which the probe operated, according to the theory of Langmuir and Mott-Smith,[6] showed that in our experiments, with E_p = 140 v, $(i_p)_0$ = 0.1 to 6 ma, the probe operated in the orbitally-limited current mode (r_{layer}/r_{probe} = 2.7 to 15). Under these conditions the current to the probe, after the velocity distribution of the positive ions and of the neutral molecules has been equalized, is proportional to the concentration of positive ions n_p. Therefore, from the shape of the curves $i_p = F(t)$, we can directly determine the rate of deionization and the quantity reciprocal to it

$$\tau = -\frac{dt}{d[\ln(n/n_0)]} = -\frac{dt}{d[\ln(i_p/i_{p0})]}.$$

The experiments were carried out in straight cylindrical experimental tubes of diameter 32 and 65 mm, of length 220 and 400 mm, with an oxide cathode. Cylindrical probes (diameter 0.8 mm, length 11 mm) were situated along the axis of the tube; the inactive parts of the probes were

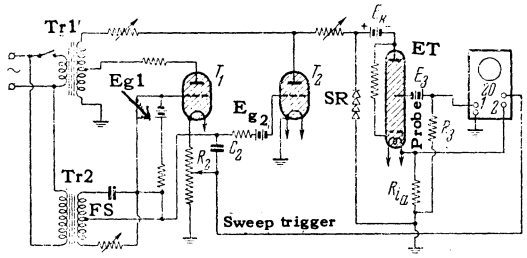

FIG. 1. Circuit for the measurement of the rate of deionization in hydrogen.

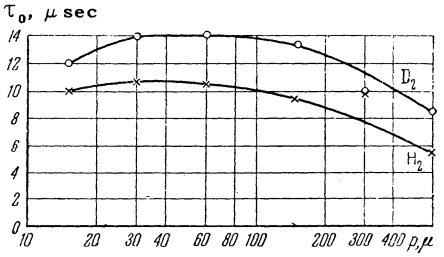

FIG. 3. The initial deionization "time-constant" τ_0 in D_2 and in H_2 as a function of the pressure; $I_0 = 0.5$ amp, d = 65 mm.

insulated from the plasma by a capillary of 1.0 mm diameter. The gases to be investigated (H_2 and D_2) were obtained by means of electrolysis H_2O or D_2O; they were first purified by means of silica gel, then by heated copper filings and, finally, by freezing in a liquid-nitrogen trap.

Mass-spectrometric analyses of the gas taken from the tube when the cathode was heated showed that D_2 contained a certain amount of H_2 and traces of other gases. This could not have significantly affected the results of the experiments. The pressure of H_2 and D_2 was varied in the course of the experiments within the range 0.015 to 0.6 mm Hg.

The electric circuit used in the experiments is given in Fig. 1. The current in the experimental tube ET was interrupted at its maximum by means of a shunting thyratron T_2. The reversed voltage was picked off ET by selenium rectifier SR connected in parallel to ET. The delayed sweep of the oscillograph (marked 20 in the diagram) was triggered by a pulse from the thyratron T_1, which through a delay circuit (C_2, R_2) also triggered the shunting thyratron T_2. To calibrate the sweep, timing markers were produced on the oscillogram every 1.2 or 5 μ sec. The vertical deflection was calibrated by a sinusoidal current (not shown in the circuit diagram), but this calibration played no role in the determination of the relative rate of deionization.

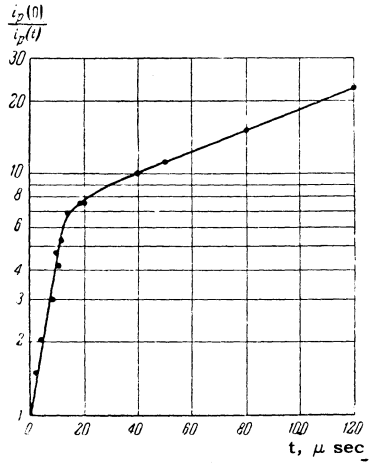

FIG. 2. The ratio $i_p(0)/i_p(t)$ shown as a function of the time. The vertical axis has a logarithmic scale.

3. EXPERIMENTAL RESULTS

(a) The shape of the probe current vs. time curve, i.e., the time dependence of the decrease in the concentration of the positive ions $n_p(t)$ for both isotopes, could be observed already 2 to 4 μ sec* after the cessation of current. As had already been shown by previous observations in Hg[2] and in H_2^+[3], this falling-off in H_2 and in D_2 takes place in a nonexponential manner. As an example, Fig. 2 shows the shape of the curve $i_p(0)/i_p(t) = f(t)$ in a tube of 65 mm diameter filled with D_2 at $p = 600\,\mu$ Hg and $I_0 = 0.9$ amp. It is clearly seen that the shape of the curve is on the whole nonexponential, but that its beginning,† and particularly its end, can be represented by exponentials with different "time-constants" τ_0 and τ_c, with $\tau_c > \tau_0$. Wherever possible we tried to determine both quantities (τ_0 and τ_c). But in contrast to the microwave method the quantity τ_0, which characterizes the rate at the beginning of the process, is determined from the probe oscillograms more reliably than τ_c, which refers to the conclusion of the process, since the initial deflections on the screen are considerably greater than those near the end.

(b) The dependence of the rate of deionization on the degree of rarefaction of the gas and on the extent of the ionized region is similar in both isotopes (H and D). This refers both to the initial rate of deionization characterized by the quantity reciprocal to τ_0, and to the rate of the process in the latest stage, i.e., to τ_c. The dependence of τ_0 on the gas pressure p can be seen in Fig. 3.

*This is one of the advantages of the probe method over the microwave method, which usually discloses the later stages of the process (after 30 to 50 μsec).

†With the exception of the first few microseconds during which the ionization of the gas ceases and the plasma starts to decay.

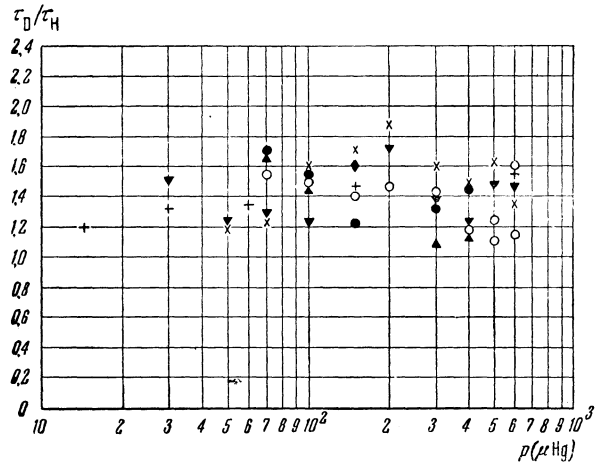

FIG. 4. The ratio of the deionization time constants in deuterium and in hydrogen τ_D/τ_H as a function of the pressure for τ_0 (initial) corresponding to ○) d= 36 mm, I_0 = 500 ma; ●) d = 65 mm; I_0 = 500 ma; +) d = 65 mm, I_0 = 60 ma; for τ_c (final) corresponding to ▲) d = 36 mm, I_0 = 1500 ma; ▼) d = 65 mm, I_0 = 1500 ma; ×) d = 65 mm, I_0 = 60 ma.

It turns out to be non-monotonic both in H_2 and in D_2, in agreement with Gavrilov's data[3] on H_2: there exists a pressure p_m for which τ_0 has a maximum value and, consequently, the deionization proceeds at the slowest rate. A similar dependence on the pressure is observed also in the latest stage of the processes.

As the diameter of the positive column is increased, the rate of deionization is considerably slowed down in the pressure range investigated by us. The minimum rate of deionization occurs at pd ~ 10^{-1} to 1 mm Hg·cm.

(c) A comparison of the rates of deionization in both isotopes (H and D) shows that both τ_0 and τ_c are larger in deuterium than in hydrogen, under all the conditions investigated by us. The ratio of the time-constants of deionization in both gases τ_D/τ_H measured with all other conditions being equal (the same d, p and I_0, and at the same stages of the process) may be taken as a characteristic quantity in this case. Figure 4 shows values of this ratio found in six series of measurements.

In spite of the considerable scatter of points (the average error of a single measurement is 0.19), they are all grouped about one mean value, 1.4 ± 0.03. It is the same both in the initial and in the final stages of the process. Also, it does not depend (at least in the first approximation) on the gas pressure within the range investigated by us. If the data referring to $p < 100\mu$ Hg and to $p > 300\mu$ Hg are treated separately, it turns out that in the latter region the average value of τ_D/τ_H is somewhat smaller and is equal to 1.3_1; however we cannot assert that this difference lies outside the experimental error.

4. DISCUSSION OF RESULTS

I. The difference in the rate of deionization at the beginning and at the end of the process, i.e., the gradual slowing down of the process with time ($\tau_c > \tau_0$) is associated, as was shown earlier, with the gradual "cooling down" of the electron gas and with the transition of the plasma from the initial nonequilibrium state (at $t = 0$, $T_e \gg T_g$) to thermal equilibrium (at $t \to \infty$, $T_e \to T_g$).[2] A decrease in T_e during the deionization stage was observed in references 7 and 8.

II. The non-monotonic dependence of τ_0 and τ_c on the gas pressure is due to the fact that as the pressure changes the relative role played by the various elementary deionization processes is altered. For $p < p_m$ [the increasing branch of the curve $\tau = f(p)$] the charge carriers primarily diffuse from the gas towards the walls where they recombine (the diffusion mode). For $p > p_m$ the volume recombination in the gas itself begins to play the principal role (the recombination mode,[2,3] cf. also reference 7). As the diameter of the column is increased the diffusion proceeds more slowly and volume recombination begins to play a greater role. Therefore for large diameters the curve $\tau = f(p)$ passes through a maximum earlier (at lower pressures).

III. Both in the diffusion and in the recombination modes, we have $\tau_D/\tau_H = 1.41$, i.e., within experimental error $\tau_D/\tau_H = (A_D/A_H)^{1/2} = (m_D/m_H)^{1/2}$ (A is the atomic weight). In the diffusion mode ($p < p_m$) we have $\tau = \Lambda^2/D_a$, where Λ is the so-called diffusion length; in the present case $\Lambda = d/2\mu$ ($\mu \leq 2.405$ is the eigenvalue of the diffusion boundary-value problem); D_a is the coefficient of bipolar diffusion,

$$D_a = b_p [T_e(V) + T_g(V)],$$

where $T_e(V)$ and $T_g(V)$ are the temperatures of the electron and the neutral gas expressed in volts.[2] At the beginning of the process $T_e(0) \gg T_g$ and $D_a \approx b_p T_e(0)$; at the end of the process $T_e \approx T_g$ and $D_a \approx 2b_p T_g(V)$. Further

$$b_p \approx e_0 \lambda_p / m_p \bar{c}_p = e_0^{1/2} \lambda_p / (2 T_g m_p)^{1/2},$$

since in the deionization stage $T_p \approx T_g$ almost from the start. The quantities T_g, λ_p, and T_e may differ somewhat in H and in D. Thus, because of the lower rate of diffusion in D_2 the mean ionization frequency z (sec^{-1}) (and consequently also the value of $T_e(0)$ in D_2) must be somewhat lower than in H_2 (cf. also references 9 and 10). Further, since the average fraction of the

kinetic energy transferred by elastic collisions between electrons and molecules, $\kappa = 2m_e/m_g$, is smaller in D_2 than in H_2, the gas temperature T_g can also be less in D_2 than in H_2. However, all these differences are small compared with the difference in the mobilities of the D and H ions; therefore in the first approximation we should expect that in the diffusion mode

$$\tau_D / \tau_H = (D_a)_H / (D_a)_D = (b_p)_H / (b_p)_D = (m_D / m_H)^{1/2} = \sqrt{2} = 1.41,$$

which is indeed observed experimentally.

A more complicated state of affairs exists in the recombination mode ($p > p_m$). Here various types of elementary recombination processes can occur: (1) those involving radiation ($M^+ + e \rightarrow M + h\nu$), (2) triple collisions involving two electrons ($M^+ + 2e \rightarrow M + e$), (3) triple collisions involving neutral molecules ($M^+ + e + M \rightarrow 2M$), (4) electron capture by a neutral molecule and the subsequent recombination of the ions ($e + M \rightarrow M^-$; $M^- + M^+ \rightarrow 2M$), and (5) dissociative recombination ($M_2 + e \rightarrow M^* + M$). The recombination coefficients in cases (1), (2) and (5) depend only on the average velocities of the electrons (i.e., on T_e) and on the effective cross sections and the statistical weights of the ions, which are also determined by T_e (cf., for example, reference 11). Consequently in the first approximation* the rate of recombination in these two cases should not depend appreciably on the atomic weight of the gas. And since experiment shows that in the recombination mode deionization occurs more slowly in D_2 than in H_2, therefore under our experimental conditions recombination plays no significant role in either double collisions [cases (1) and (5)] or triple collisions with two electrons. Conversely, the third and the fourth processes enumerated above both lead to the required result. The recombination coefficient β in the third case is proportional to the average velocity of the gas molecules; in the fourth case it is proportional to the average velocity of the ions. In both cases $\beta \sim (m_g)^{1/2}$ and, consequently, one can expect that $\tau \sim A^{1/2}$. The choice between the third and the fourth process under our experimental conditions is facilitated by estimating the mean time for the capture of electrons by molecules:

$$\tau_{capt} = (s_{capt} \bar{c}_e \cdot n_g)^{-1}.$$

The literature contains data on the calculated values of s_{capt} for H atoms:[12] $s_{capt} \sim 10^{-22}$ cm^2. To obtain an upper limit for the estimate of the capture cross section for the H_2 and D_2 molecules, we take a value greater by an order of magnitude: 10^{-21} cm^2. Further we set $\bar{c}_e = 10^8$ cm/sec; at the highest pressure investigated by us ($p = 0.6$ mm Hg) $n_g = 2 \times 10^{16}$ cm^{-3}; then $\tau_{capt} \sim (10^{-21} \times 10^8 \times 2 \times 10^{16})^{-1} = 0.5 \times 10^{-3}$ sec $= 500\,\mu$ sec. Since the deionization process in our experiments occurred mainly during a time ≤ 30 to $50\,\mu$ sec, the formation of negative ions could not have played any significant role in this case. Consequently the principal recombination process under the above conditions is recombination in a triple collision involving a neutral molecule.

*Neglecting the small difference of T_e in H_2 and D_2, which has been already noted above.

5. CONCLUSIONS

1. The process of plasma deionization occurs in deuterium at a rate which is 1.4 times slower than in hydrogen over the whole range of conditions investigated by us (pressures from 15 to $600\,\mu$ Hg, tube diameters 3.2 and 6.5 cm, preceding current from 60 to 1500 ma). This ratio is equal to the square root of the ratio of the molecular weights of the two gases.

2. For $pd \leq 10^{-1}$ mm Hg·cm deionization occurs primarily by means of the diffusion of charged particles to the walls where they recombine.

3. For $pd \geq 1$ mm Hg·cm volume electronic recombination is predominant in the process of deionization of hydrogen and deuterium. The principal elementary process is now recombination in triple collisions involving a neutral molecule.

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