Physical Chemistry

Academician of the Academy of Sciences of the Uzbek SSR S. V. Starodubtsev, V. M. Knopov, S. L. Pozharov, I. G. Chernov

1965

SovietRxiv

Abstract

Full Text

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On the Existence of the Ion H_5^+ in the Positive Column of a Hydrogen Glow Discharge at Elevated Pressure

In recent years a number of works have been undertaken (1-3) on the mass-spectrometric study of ionic species formed in a gas-discharge plasma. In most cases, ions ambipolarly diffusing to the walls of the discharge chamber from a stationary glow discharge burning at pressures of 0.1-1.0 mm Hg were studied. The general result of these investigations was the discovery of a relatively high efficiency of formation of heavy molecular ions, which the authors called ionic clusters.

The most surprising report was that of Dawson and Tickner, who, while studying the negative glow of a hydrogen discharge at a pressure of 0.25 mm Hg (4), detected the cluster H_5^+. This ion had not been observed previously, and, despite the fact that it had been predicted theoretically (5), its existence seemed doubtful. At the same time, the existence of the ionic cluster $H_3^+ \cdot H_2$ was proposed by Sheffer and Thompson (6) as a possible intermediate product of hydrogen-deuterium exchange induced by irradiation.

Using the apparatus described earlier (7), we studied the positive column of a glow discharge in hydrogen at higher pressures. The ions were sampled from the plasma along the axis of the discharge through a hole in the anode of diameter $72\,\mu$.

Before the beginning of each series of measurements the chamber and the inlet system were heated for two hours at a temperature of about 200° under continuous pumping.

The insignificant contribution of impurity ions to the overall mass spectrum indicated that the degree of cleaning of the chamber was satisfactory. The pressure in the vestibule volume in all measurements did not exceed $5 \cdot 10^{-5}$ mm Hg. In the analytical part of the instrument the pressure remained equal to $3 \cdot 10^{-6}$ mm Hg.

Along with the ions H_1^+, H_2^+, and H_3^+, we detected an ion with mass number 5, whose current intensity, relative to the current of H_3^+ ions, at a pressure of 5 mm Hg was 0.65%, which is five times greater than the analogous value measured in work (4). The accuracy of the measurement in this case was not worse than 5%. Thus, the identification of this ion with the cluster H_5^+ is beyond doubt. In

Fig. 1. Dependence on pressure of the relative ion current of (1) H_5^+ and (2) H_4^+. Point A corresponds to the relative ion current of H_5^+ measured in work (4).

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addition, an ion with mass number 4 was observed, which may be assigned to H_2D^+, owing to its insignificant content.

The high sensitivity of the apparatus used and the relatively large intensity of the ion current extracted from the discharge ($\sim 4 \cdot 10^{-8}$ A) made it possible to measure with sufficient accuracy the dependence of the relative current intensity of H_5^+ ions on the pressure and discharge current.

Curve 1 of Fig. 1 conveys the character of the dependence of the relative current of H_5^+ ions on pressure. The large value of the root-mean-square error is explained by the result of dividing one imprecise quantity (the current of H_5^+ ions) by another (the current of H_3^+ ions). Nevertheless, on the curve still···

shows a noticeable minimum at 7 mm Hg, then an increase to a maximum at a pressure of 9 mm Hg, followed by a sharp drop at 10 mm Hg. Point A on the graph corresponds to the relative current of H_5^+ ions measured in work (4).

Curve 2 pertains to the ion with mass number 4. The form of the curve apparently can be explained by the effect of "isotopic enrichment" (8) and by its dependence on pressure.

Fig. 1. Dependence on pressure of the relative ion current of (1) H_5^+ and (2) H_4^+. Point A corresponds to the relative ion current of H_5^+ measured in work (4).

The absence of any information concerning the H_5^+ ion does not allow us to interpret the results presented here with sufficient unambiguity. However, purely qualitatively, the dependences obtained can be explained as follows. With increasing pressure, the number of triple collisions increases, in which, in all probability, the complex $H_3^+ \cdot H_2$ is formed:

$$H_2^+ + 2H_2 = H_3^+ \cdot H_2 + H_2.$$

On the other hand, an increase in pressure is associated with a decrease in the electron temperature and an increase in the concentration of free electrons, and this, in turn, must be associated with an increase in the probability of volume recombination of the H_5^+ ion with electrons. It must be supposed that the coefficient of volume recombination for the H_5^+ ion should be very high. The action of these two competing processes can explain the formation of a maximum in the pressure range 4–9 mm Hg.

The supposition of the high efficiency of volume recombination of the H_5^+ complex with electrons is in good agreement with the dependence we obtained of the relative current of this ion on the discharge current, from which it follows that, with increasing discharge current, the relative current of H_5^+ falls rather rapidly.

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Received
22 I 1965

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Note: Figure translations are in progress. See original paper for figures.