IONIC COMPOSITION OF THE POSITIVE COLUMN OF A GLOW DISCHARGE IN INERT GASES AT ELEVATED PRESSURE

PHYSICS

1966

SovietRxiv

Abstract

Full Text

UDC 537.525

PHYSICS

Academician of the Academy of Sciences of the Uzbek SSR S. V. STARODUBTSEV, S. L. POZHAROV, I. G. CHERNOV,
V. M. KNOPOV

IONIC COMPOSITION OF THE POSITIVE COLUMN OF A GLOW DISCHARGE IN INERT GASES AT ELEVATED PRESSURE

In the study of ionization in a glow discharge ([1]) it was established that, at pressures above 5 mm Hg, conditions are created that are favorable for the formation and stabilization of complex cluster ions, which at lower pressures, as a rule, are either not observed or are observed in substantially smaller amounts.

In the present article we report some results of an investigation of glow discharges in inert gases with an admixture of mercury vapor in the pressure range from 5 to 50 mm.

The measurements were carried out on a mass spectrometer specially designed for studying ionic processes in the gas phase at high pressures ([2]). The discharge in helium and argon was studied. In both cases the partial pressure of mercury was about 10^{-3} mm. The helium was first subjected to adsorption purification with silica gel cooled by liquid nitrogen.

The absolute intensities of the ionic currents extracted through an opening in the anode, in the case of argon, depend in a complicated way on the pressure and discharge current; this dependence is, in all probability, explained by the spatial nonuniformity of the positive column and by the motion of striations relative to the anode as the pressure and discharge current change ([3]). In the helium discharge the nonuniformity is absent, which testifies to the good degree of purification of this gas.

A general regularity of ionization in the anode region may be considered to be the decrease in the concentration of the primary ion with increasing pressure, evidently associated with the increasing role of ionization of impurities by excited atoms of the principal gas as the partial pressures of impurity gases increase. Beginning at a certain point, this process may become predominant, since the necessary ionization in the positive column will be maintained only by impurities whose ionization potential is lower than the excitation potential of the principal gas.

In the argon discharge, ions with mass numbers 40, 80, and 202 are readily interpreted as Ar^+, Ar_2^+, Hg^+. The resolving power is insufficient for complete resolution of all mercury isotopes, but the peaks 200, 202, and 204 are distinctly visible. A very small amount of ArH^+ ions proved unexpected.

Of greatest interest is the peak corresponding to mass number 404, having an intensity of 1% relative to the Ar^+ ion peak. The 404 peak was first observed by Norton ([5]) in the ion source of a mass spectrometer at a mercury-vapor pressure of $\sim 2 \cdot 10^{-5}$ mm. Its magnitude was about 0.023% relative to the 202 peak. The author interpreted this peak as the result of the conversion of a doubly ionized mercury ion into a singly ionized ion in the process of charge exchange in the accelerating system of the mass spectrometer.

In our case, owing to the high intensity of the 404 peak, such an explanation is clearly unsuitable, especially since doubly ionized mercury ions were not observed at all. To assume that this is some kind of complex

formation, say, of organic origin, is also difficult, since in the mass interval from 80 to 202 there are no appreciable peaks of any kind. We therefore identified it as the molecular mercury ion Hg_2^+. In the helium discharge this ion was not detected. Here, attention is drawn first of all to the peaks with mass numbers 9 and 12, having intensities, respectively, of 0.04 and 20% relative to the He^+ peak.

The rather large content of the ion with mass number 9, its existence in a limited pressure range, and also its absence in measurements with other gases give grounds for supposing that this is a complex of the type He_2H^+. The addition of 2% hydrogen to helium leads to its disappearance. At the same time the intensity of the He_2^+ ion decreases by approximately a factor of 10.

It is more difficult to interpret the second peak. Studying the afterglow of a low-pressure helium discharge, Fite et al. [(6)] observed an ion with mass 12. They suggested that this is more likely the He_3^+ ion than a carbon ion. The circumstance that, in our measurements, the intensity of the peak with mass number 12 exceeds the total intensity of all impurity peaks that could be due to carbon compounds inclines us to this point of view.

Formation of the molecular mercury ion may occur either in the Hornbeck-Molnar process [(1)]

$$\mathrm{Hg}' + \mathrm{Hg} \rightarrow \mathrm{Hg}_2^+ + e^-,$$

or in a three-particle collision

$$\mathrm{Hg}^+ + \mathrm{Hg} + \mathrm{Ar} \rightleftarrows \mathrm{Hg}_2^+ + \mathrm{Ar}.$$

The ion He_2H^+ most probably appears in the reaction

$$He_2^+ + XH \rightleftarrows He_2H^+ + X,$$

where XH is any hydrogen impurity, including hydrogen.

The competing reaction

$$He_2^+ + XH \rightarrow HeH^+ + He + X$$

was proposed by Pahl and Weimer [8]; moreover, it is considerably more effective, and therefore a small addition of hydrogen in our experiments led to a sharp decrease in the concentration of He_2^+ and, correspondingly, He_2H^+.

It turned out that the ratio of the current of the ion with mass 12 to the current of the He_2^+ ion does not depend on pressure and increases linearly with increasing discharge current. If this ion is identified with the He_3^+ complex, then, to explain the results obtained, it is necessary to assume the following series of reactions taking place in the discharge:

$$He + e^- \rightarrow He^- + e^-; \quad (1)$$

$$He' \rightarrow He + h\nu; \quad (2)$$

$$He' + Z \rightarrow Z^+ + He + e^-; \quad (3)$$

$$He' + He \rightarrow He_2^*; \quad (4)$$

$$He_2^* \rightarrow He_2^+ + e^-; \quad (5)$$

$$He_2^* + He \rightarrow He_3^+ + e^-; \quad (6)$$

$$He_2^+ + e^- \rightarrow He' + He; \quad (7)$$

$$He_3^+ + X \rightarrow X^+ + 3He. \quad (8)$$

Here Z denotes a molecule of an impurity gas, whose partial pressure is connected with the pressure of the gas admitted.

The reaction of formation of the excited quasimolecule He_2^* (4) is assumed by us to be an intermediate one, which can then proceed along two channels: either (5), or (6).

The main losses of molecular ions He_2^+ occur through volume recombination with electrons (7), and those of He_3^+ ions through interaction with the impurity X (8). Thus, we are forced to assume that (8) has a considerably greater efficiency than the volume recombination of the He_3^+ ion with an electron. In addition, (8) may be regarded as dissociation caused by collision with a neutral helium atom

$$He_3^+ + He \rightarrow He^+ + 3He, \tag{9}$$

but this can be the case only if the dissociation energy of He_3^+ is very small.

The solution of the kinetic equations for the sequence of reactions (1)–(8) gives the following relations between the concentrations of the corresponding ions:

$$\frac{\left[He_3^+\right]}{\left[He_2^+\right]} = \frac{1}{\lambda}\frac{k_6 k_7}{k_5 k_8}\left[e^-\right],$$

$$\left[He_3^+\right] = \frac{\beta p^2}{\alpha_2 p^2 + \alpha_1 p + \alpha_0}\left[e^-\right],$$

where k_5, k_6, k_7, k_8 are the constants of reactions (5), (6), (7), and (8); λ is the ratio of the concentration of impurity X to the concentration of He; $[e^-]$ is the electron concentration; p is the pressure in the discharge chamber; $\beta, \alpha_1, \alpha_2, \alpha_0$ are coefficients depending on the constants of reactions (1)–(8).

If, however, peak 12 is assigned to the ion C^+, then it should be considered that this ion is formed as a result of the reaction of a carbon impurity with the excited quasimolecule. Then, in the sequence of reactions (1)–(8), processes (6) and (8) must be replaced by

$$He_2^* + YC \rightarrow C^+ + Y + 2He, \tag{6'}$$

$$C^+ + X \rightarrow CX_1^+ + X_2. \tag{8'}$$

A high concentration of C^+ ions and the absence of other channels for the reaction of the carbon impurity with the excited quasimolecule may occur in the case of resonance in reaction (6′), i.e., if the appearance potential of the C^+ ion from the impurity YC is close to the energy of the excited quasimolecule.

For the final identification of peak 12, control experiments were carried out. The influence on the magnitude of the peak of a change in temperature in the discharge chamber and of the addition of carbon dioxide gas to helium was determined. It turned out that heating the chamber to a temperature of the order of 100° practically does not affect the intensities of all peaks, while a small addition of carbon dioxide gas leads to a sharp decrease in the ion current with mass 12, as well as of the ions He_2^+ and He^+. In addition, on the side of light masses of peak 12 there appears a weak shoulder, whose height varies with pressure. The formation of this shoulder is, in all probability, connected with the superposition of the peaks of He_3^+ and C^+, the difference in whose mass numbers is approximately 0.008 a.m.u., while the width of the He_3^+ peak in atomic mass units was 0.09. Thus, the shoulder should be equal to 0.1 of the peak width, which corresponds to the observed pattern.

Institute of Nuclear Physics
Academy of Sciences of the Uzbek SSR

Received
11 X 1965

CITED LITERATURE

1. S. V. Starodubtsev, S. L. Pozharov, I. G. Chernov, V. M. Knopov, DAN, **163**, No. 1, 155 (1965).
2. K. S. Burdin, S. L. Pozharov, D. S. Starodubtsev, I. G. Chernov, Izv. AN UzSSR, **4**, 59 (1963).
3. H. Drost, U. Timm, H. Pupke, Proc. V Intern. Conf. Ion. Phenom. in Gases, **1**, 1961.
4. P. F. Knewstubb, A. W. Tickner, J. Chem. Phys., **36**, 674 (1962).
5. F. J. Norton, Nat. Bur. Stand. U.S. Circ. **522**, 201 (1953).
6. W. L. Fite, J. A. Rutherford et al., Disc. Farad. Soc., **33**, 264 (1962).
7. A. Hornbeck, J. P. Molnar, Phys. Rev., **84**, 621 (1951).
8. M. Pahl, U. Weimer, Proc. IV Intern. Conf. Ion. Phenom. in Gases, **1**, 1960, p. 293.

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