acta phys. slov. 27. (1977), No. 3

CONTRIBUTION TO AN EXPLANATION OF A RETROGRADE CATAPHORESIS PROCESS

JOZEF TRNOVEC,* Bratislava

A physical principle of the retrograde cataphoresis process is somewhat reconsidered from the point of view of segregation processes of gas components in binary mixtures. In the present paper this process is described in a new way, where the momentum equations for plasma components are utilized. The present conclusions are in a good agreement with experimental data recording this process in nonpenning mixtures.

ВКЛАД В ОБЪЯСНЕНИЕ РЕГРЕССИРУЮЩЕГО КАТАФОРЕЗНОГО ПРОЦЕССА

Физический принцип регрессирующего катафорезного процесса немного пересматривается с точки зрения процессов разделения компонентов газа в двухкомпонентных смесях. В настоящей статье этот процесс описывается по-новому, причём используются уравнения моментов для компонент плазмы. Представление выводы находятся в хорошем согласии с экспериментальными данными, регистрирующими этот процесс в непеннинговых смесях.

I. INTRODUCTION

Generally, in a d.c. discharge plasma, the cataphoresis processes are investigated in the Penning mixtures, where the admixture gas, with a lower ionizing potential than a metastable energy level of the main gas, is cumulated in the cathode space. Druyvesteyn [1] explained this effect by a strong flow of the admixture ions as a result of the Penning ionization. In a steady state this flow is equal to the admixture neutral atoms flow, but in the opposite direction. Druyvesteyn's theory was improved by many physicists. Now there exist the exact description of the time and space dependences of this segregation process. The mentioned access to the cataphoresis processes cannot explain an increase of the admixture atoms density in the anode space (retrograde cataphoresis), which was reported in the papers of Kenty [2] and Schmeltekopf [3]. Kenty [2] explained qualitatively this effect by the selective pressure of the electrons on the admixture atoms. Freudentahl [4] calculated the momentum transfer by electrons and ions to the admixture gas, but some assumptions in this method are not sufficiently explained.

In the present paper a new method is used to calculate the force due to the momentum transfer by electrons and ions to admixture atoms. The utilized simplified assumptions are discussed. Direction of this force is calculated for two mixtures and the obtained results are compared with the experimental data [2], [3].

II. METHOD

When an externally applied force $\vec{F}_i$ acts on particles of type i, the momentum equation (the force equation) related to particles of this type can be written [5]:

$$\frac{\partial}{\partial t}(m_i n_i \vec{v}_i) + \nabla(m_i n_i \overleftarrow{v_i} \vec{v}_i + \vec{p}_i) - n_i \vec{F}_i = \sum_t \vec{P}_{it} + \vec{P}_i^{\,i} \qquad (1)$$

where m_i, n_i and $\vec{v}_i$ are mass, number density and drift velocity of type i particles, $\vec{p}_i$ is the tensor of the kinetic pressure, $\vec{P}_{it}$ represents the momentum lost (obtained if $\vec{P}_{it} > 0$) per unit volume per second by the particles of group i as a consequence of elastic collisions with particles of type t. This term is the force exerted per unit volume by particles of group t on particles of group i. The force $\vec{P}_{it}$ is given [5]:

$$\vec{P}_{it} = -m_i n_i \nu_{it}(\vec{v}_i - \vec{v}_t) \qquad (2)$$

where ν_{it} is the collision frequency for the momentum transfer of type i particles with a group of particles of type t, $\vec{v}_t$ is the drift velocity of the particles of the group. The term $\vec{P}_i^{\,i}$ is the momentum which particles of type i obtain per unit volume in inelastic collisions.

In a nonpenning gas mixture the number ion density of the main gas is by several orders larger than the number density of the admixture ions. Therefore, in the following only the ions of the main gas are considered.

In the steady state Eq. (1) gives for the admixture neutral atoms:

$$\nabla \cdot (m_2 n_2 \overleftarrow{v_2} \vec{v}_2 + \vec{p}_2) = \vec{P}_{2,1} + \vec{P}_{2,e} + \vec{P}_{2,i} + \vec{P}_2^{\,i} = \vec{F}_d \qquad (3)$$

where the subscripts 1, 2, e and i indicate the main neutral gas, the admixture neutral gas, electrons and ions, respectively, $\vec{F}_d$ is a spatial dependent force, which will be called the driving force on the admixture neutral atoms. The term $\vec{P}_{1,2}$ can be neglected, because in the steady state, the neutral atom drift velocities are very

* Katedrá experimentálnej fyziky PFUK, Mlynská dolina, CS-816 31 BRATISLAVA

small in comparison with the drift velocities of the charged particles. The term $\vec{P}_2^i$ is directly proportional to the loss or gain rate of the admixture neutral atoms. In the nonpenning and chemically inert mixture this term is very small in comparison with $\vec{P}_{2,e}$ and $\vec{P}_{2,i}$. The driving volume force $\vec{F}_d$ is due afterwards to the momentum transferred by electrons and ions to the admixture neutral atoms:

$$\vec{F}_d = \vec{P}_{2,e} + \vec{P}_{2,i} = -(\vec{P}_{e,2} + \vec{P}_{i,2}). \tag{4}$$

Hence the combination of Eq. (4) and Eq. (2), with the assumption that the neutral atoms drift velocities can be neglected gives

$$\vec{F}_d = m_e n_e \nu_{e,2} \vec{v}_e + m_i n_i \nu_{i,2} \vec{v}_i , \tag{5}$$

where $\nu_{e,2}$ and $\nu_{i,2}$ are collision frequencies of the electrons with the admixture atoms, $\vec{v}_e$ and $\vec{v}_i$ are the drift velocities of the electrons and ions in the gas mixture. Generally, the driving volume force $\vec{F}_d$ is not equal to zero, but there do not exist experimental data for the calculation $\vec{F}_d$ by Eq. (5). Therefore we will modify this equation in the following way.

For the drift velocities we use: $\vec{v}_e = K_e\vec{E}$, $\vec{v}_i = K_i\vec{E}$, where K_e, K_i are the electron and ion mobilities in the mixture, respectively, $\vec{E}$ is the electric field. In the mixtures, in which the main neutral gas pressure p_1 is some orders higher than the admixture gas pressure p_2, the mobilities are determined by the main gas. Therefore K_e, K_i are afterwards the mobilities in the main gas. If K, ν are the mobility and collision frequency referred to the pressure p and K^r, ν^r are these quantities referred to 760 torr and to the same neutral gas temperature, there are valid the following expressions

$$K = K^r 760/p \tag{6a}$$

$$\nu = \nu^r p/760. \tag{6b}$$

We use Eqs. (6) for $\nu_{i,2}$, $\nu_{e,2}$ and $K_{i,1}$, $K_{e,1}$. Then the force $\vec{F}_d$ is given by

$$\vec{F}_d = \vec{E}\frac{p_2}{p_1}(m_i n_i \nu^r_{i,2} K_{i,1} - m_e n_e \nu^r_{e,2} K^r_{e,1}). \tag{7}$$

Equation (7) is physically intelligible, but further arrangements are necessary in order to obtain an equation which could be numerically solved.

If the assumption is valid that an electric field and a viscosity force of the neutral gas are the only forces acting on the electrons and ions, the following expression for $\nu^r_{e,1}$, $\nu^r_{i,2}$ can be obtained from the force equations:

$$\nu^r_{e,1} = e/m_e K^r_{e,1} \tag{8a}$$

$$\nu^r_{i,2} = e/m_i K^r_{i,2}. \tag{8b}$$

The substitution of Eq. (8) into Eq. (7) is correct if the electron motion is determined by collisions with the main gas and Blanc's law is valid for admixture ions. After this substitution $\vec{F}_d$ is given by

$$\vec{F}_d = \vec{E}_e \frac{p_2}{p_1}\left(n_i \frac{K^r_{i,1}}{K^r_{i,2}} - n_e \frac{\nu^r_{e,2}}{\nu^r_{e,1}}\right). \tag{9}$$

The chaotic velocity of the electrons is by some orders larger than the drift velocity, therefore $\nu_{e,2}/\nu_{e,1} = \sigma_{e,2}/\sigma_{e,1}$, where $\sigma_{e,2}$ and $\sigma_{e,1}$ are the momentum transfer cross sections of electrons with the admixture and the main atoms. The define form for $\vec{F}_d$ is given by:

$$\vec{F}_d = \vec{E}e \frac{p_2}{p_1}\left(n_i \frac{K^r_{i,1}}{K^r_{i,2}} - n_e \frac{\sigma_{e,2}}{\sigma_{e,1}}\right). \tag{10}$$

From this equation we see that the force $\vec{F}_d$ increases if the number density of the electrons and ions, the electric field $\vec{E}$, the ratio p_2/p_1 and the term

$$M = n_i \frac{K^r_{i,1}}{K^r_{i,2}} - n_e \frac{\sigma_{e,2}}{\sigma_{e,1}} \tag{11}$$

are increased. In the case when the vectors $\vec{F}_d$, $\vec{E}$ are parallel the admixture atoms are transported to the cathode, if $\vec{F}_d$ and $\vec{E}$ are antiparallel, the admixture atoms move to the anode. The direction of $\vec{F}_d$ is determined by the sign of M. The value of M is dependent on the efficiency of the momentum transfer from ions and electrons to the admixture and the main neutral atoms.

Substitution of Eq. (10) into Eq. (3) and the integration of this equation leads to spatial distribution of the admixture neutral atoms. For the realization of this procedure it is necessary to know the space dependences of the number densities n_i n_e and the electric field $\vec{E}$ (the term M changes slightly). These dependences are different in various gases and in various experimental conditions, we therefore calculate in the following discussion only the term M.

III. RESULTS AND DISCUSSION

First we determine the direction of the driwing force in the positive collum (i.e. $n_e = n_i$) for the mixtures of Ne with an admixture of He. In these mixtures the retrograde cataphoresis process was experimentally investigated [3]. We calculate the term M for identical experimental conditions, i.e. the discharge current 200 mA, the neutral gas pressure 27 torr, the diameter of the discharge tube roughly 1 cm. Under these conditions the Ne_2^+ ions dominate, i.e. $K'_{i,1}$ and $K'_{i,2}$ are the reduced mobilities of Ne_2^+ in neon and helium. The used values were obtained from [6], $K'_{i,1} = 6.5$ cm^2/Vs, $K'_{i,2} = 25$ cm^2/Vs, after the electron energy has been determined from the dependence of the electron temperature T_e on pR for neon [7]. T_e is 1.9×10^4 K, which means that the electron energy is 1.66 eV. The quantities $\sigma_{e,1}$ and $\sigma_{e,2}$ were obtained from the dependences σ on the electron energy [8], $\sigma_{e,1} = 1.7 \times 10^{-16}$ cm^2, $\sigma_{e,2} = 7 \times 10^{-16}$ cm^2. The ratio $K'_{i,1}/K'_{i,2} < 1$, i.e. the momentum transfer by ions Ne_2^+ to helium is small. On the other hand the momentum transfer by electrons to the helium atoms is large, because $\sigma_{e,2}/\sigma_{e,1} > 1$. The value of the term M is $-3.86n$ and therefore $\vec{F}_d$ has the direction to the anode, where the helium atoms are accumulated. This conclusion is in agreement with the results presented in the paper of Schmeltekopf [3] for mixtures of 99 % Ne with 1 % He and 52 % Ne with 48 % He.

Most of experimental data about the retrograde cataphoresis are in paper [2], where this process was investigated in the mixture of Xe with Hg vapours. The mercury vapours were accumulated in the anode space for discharge currents higher than 1 A. In this mixture the momentum transfer by electrons to Hg vapours is very effective (there is no Ramsauer effect in Hg), on the other hand the momentum transfer by electrons to Xe atoms is small (due to the Ramsauer effect in Xe). The ratio $K'_{i,1}/K'_{i,2}$ is roughly 0.8 if $K'_{i,1}$ is the mobility of the X_e^+ ions in Xe [6], $K'_{i,2}$ is the mobility of the Xe_2^+ ions in Hg calculated by the Langevin formula. Then, the momentum transfer by Xe_2^+ ions to the Hg vapour is very small. According to [6] and [8] certainly $\sigma_{e,2}/\sigma_{e,1} > 1$ for the electron energy interval 1—4 eV. The term M is negative for this mixture, we assume that the force $\vec{F}_d$ has the direction to the anode. It was further observed that the separation speed increases if the discharge current increases. This effect is also in agreement with our theory (see Eq. (10)), assuming that the number density of the electrons and ions increases more rapidly than $\vec{E}$ decreases, when the discharge current is increased.

It is necessary to remark that in this mixture there was observed an accumulation of the Hg vapour in the cathode space if the discharge current was smaller than 1 A. We explain it by the presence of Hg^+ ions in the discharge, as the result of the small difference between the ionizing potentials of xenon and mercury vapour. The Hg^+ ions are drifting to the cathode, the result is determined by the sum of this current and the drift current of the Hg atoms to the anode.

IV. CONCLUSION

By the present simple theory of the retrograde cataphoresis process the driving force can be determined which is due to the momentum transfer by electrons and ions to the admixture neutral atoms in various gas mixtures. This theory is the starting point of the exact solution of the macroscopical equations which take into consideration the spatial dependences of the used quantities.

V. ACKNOWLEDGEMENTS

The author wishes to express his appreciation to V. Martišovitš, P. Lukáč and T. Šipőcz for valuable advice and helpful discussions.

REFERENCES

[1] Druyvesteyn M. J., Physica *2* (1935), 255.
[2] Kenty C., J. Appl. Phys. *38* (1967), 4517.
[3] Schmeltekopf A., J. Appl. Phys. *35* (1964), 1712.
[4] Freudentahl J., Physica *36* (1967), 354.
[5] Allis W. P., Fluge S., *Handbuch der Physik Vol. 21.* Ed. Springer-Verlag, Berlin 1956.
[6] McDaniel E. W., *Processy stolknovenij v ionizovynnych gazach.* Izd. Mir, Moskva 1967.
[7] Granovskij V. L., *Elektročeskij tok v gaze.* Izd. Nauka, Moskva 1971.
[8] Barbiere D., Phys. Rev. *84* (1951), 654.

Received September 1st, 1976