CATAPHORESIS AND COLLISION PROCESSES IN LOW-PRESSURE DISCHARGES

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Synopsis

The cataphoretic segregation was measured in Ne–Ar and He–Ne mixtures by means of a mass spectrometer. The dependence of the segregation on the tube current and total gas pressure appeared to be consistent with theory. The segregation in Ne–Ar was measured as a function of the percentage of admixed Ar and as a function of the gas temperature.

Measurements in He–Ne were performed as a function of the percentage of admixed Ne and as a function of the total pressure. From this we arrived at the following reactions in this plasma for pressures of about 5 torr: $He^+ + 2He \rightarrow He_2^+ + He$ and $He_2^+ + Ne \rightarrow Ne^+ + 2He$.

Introduction. In a former paper[1]) the transports were discussed that led to a segregation in a DC-discharge in a mixture of gases[2]).

The choice of the gas mixtures was such that only field transport of ions and diffusion of atoms have to be considered. The gas mixtures used were Ne with a small admixture of Ar and He with a small admixture of Ne. In these two mixtures the admixture gas is ionized relatively strongly. Consequently the ion transport of the admixture gas is relatively great. Moreover, the momentum transfer of the electrons and ions to the admixture gas is small. Therefore the transport due to selective momentum transfer is negligible compared to the ion transport[2]).

The segregation itself can be measured spectroscopically[3–7]) or mass-spectrometrically. In our experiments we used the mass-spectrometrical method to determine the distribution of the gases along the positive column of the discharge.

Below we shall compare the experimental results with the theory and we shall further draw some conclusions about elementary collision processes in the plasmas.

1. *Experimental method.* The distribution of the gases along the positive column of the discharge (tube length = 129 cm, inner diameter 2.4 cm) was

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determined by sampling some gas at several places in the positive column. This gas was analysed in a mass spectrometer (see fig. 1). Three molecular gas leaks were mounted in the wall of the tube to sample the gas. Since the discharge tube contains a cathode and anode on each side of the tube the discharge could be reversed; in this way the composition of the gas could be determined at six places in the positive column with three leaks. A furnace was placed around the tube for two purposes: first to bake the tube during pumping and secondly to regulate the gas temperature of the discharge (in temperature dependent experiments). Moreover, a refrigerator system could be inserted in the "furnace" to cool the discharge (during temperature dependent experiments). The gas mixtures were supplied in glass vessels by the Philips gas plant. The purity of the gas was stated to be better then 0.1%. The total gas pressures in the discharge tube were measured with an Atlas membrane manometer type MCT. We used normal high vacuum glass valves (with grease).

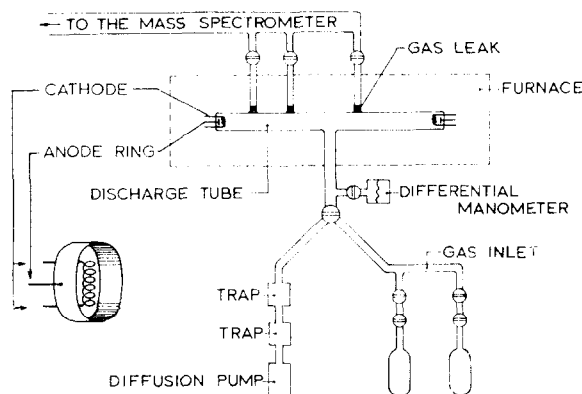All measurements, described here, of the cataphoresis were made in the stationary state.

Fig. 1. Schematic diagram of the experimental arrangement for measuring the cataphoresis in mixtures of gases. The actual electrode geometry is represented in the inset.

2. *Experimental results in Ne–Ar. a.* The axial gradient of the argon as a function of the percentage of admixed argon. The gradient of the density of the Ar $(d/dx\, n_{Ar})$ in the stationary state is given by:

$$D\, \frac{d}{dx}\, n_{Ar} = \mu_{Ar}^{+} n_{Ar}^{+} E, \tag{1}$$

with D as the diffusion coefficient, μ_{Ar}^{+} as the mobility of the Ar^{+}-ion in the gas, n_{Ar}^{+} as the density of the Ar^{+}-ions and E as the axial electric field strength. Substitution of $n_{Ar}^{+} = \alpha n^{+} \approx \alpha n^{-}$ and $n^{-} = J/\mu^{-}eE$, with n^{+} as the total ion density, n^{-} as the electron density, J as the tube current density,

α the fraction of Ar^+-ions and e as the electronic charge, gives:

$$\frac{d}{dx} n_{Ar} = \frac{\mu_{Ar}^+ \alpha J}{D\mu^- e}.$$ (2)

In a good approximation the factor $\mu_{Ar}^+ J/D\mu^- e$ in formula (2) does not depend on the argon percentage, assuming that the argon percentage is not too high (maximally a few percents). The fraction α depends on the percentage of admixed argon. A measurement of the gradient (d/dx) n_{Ar} as a function of the percentage admixed argon leads to a determination of the fraction α as a function of the argon percentage. Measurements concerning this relation have been performed also by Pahl and Weimer[8]).

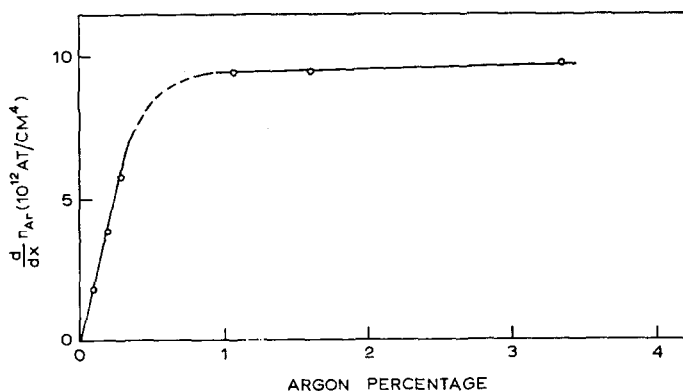Fig. 2. The axial gradient of the argon density (d/dx) n_{Ar}, as a function of the local percentage admixed argon during the measurement in a neon-argon discharge. The reduced gas pressure was 2.18 torr, the tube current 0.30 A, and the average gas temperature 335°K.

The gradient (d/dx) n_{Ar} shows an asymptotic behaviour for higher percentages of argon. This indicates that at higher percentages of argon ($> 1\%$), all ions are argon ions ($\alpha \rightarrow 1$, see fig. 2). At a low percentage of argon ($< 0.3\%$) a proportional relation exists between the gradient (d/dx) n_{Ar} and the argon percentage (or $n_{Ar}^+ = \theta n_{Ar}$, in which θ depends on the electron temperature and the tube current density, but not on the density n_{Ar}).

In mixtures with 1% argon the axial distribution is linear (see fig. 3) and in mixtures with a low percentage the distribution is exponential (see fig. 4). This is in agreement with the theory[1]).

The very strong ionization of the argon originates mainly from the ionization of the argon in impacts with neon metastable atoms:

$$Ne^m + Ar \rightarrow Ar^+ + Ne + e,$$
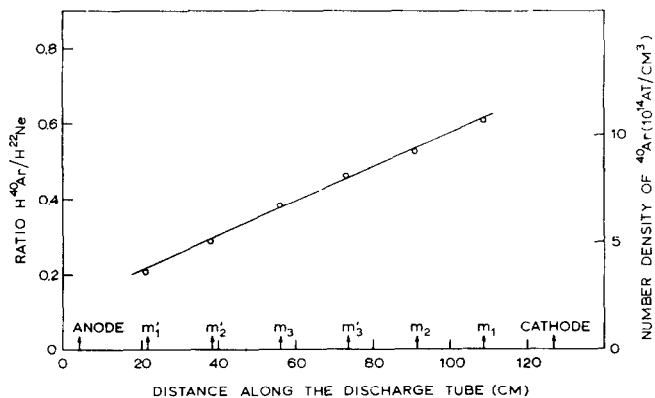
the Penning reaction[9]).

Fig. 3. An example of the cataphoresis in the stationary state in a mixture of neon with initially 1.07% argon at a total reduced pressure of 2.10 torr. The average gas temperature was 354°K and the tube current was 0.30 A. The ratio of the mass-spectrometrical peak heights of ^{22}Ne and ^{40}Ar is given as a function of the location in the discharge tube. Since we cannot distinguish between the ^{40}Ar^{++}-ion and the ^{20}Ne^{+}-ion in the mass spectrometer, the ^{22}Ne-isotope was measured in the Ne–Ar mixtures. The linear relation is in good agreement with the theory assuming that nearly all ions are argon ions. The locations of the mass-spectrometrical sampling tubes are denoted by m_1, m_1', etc.
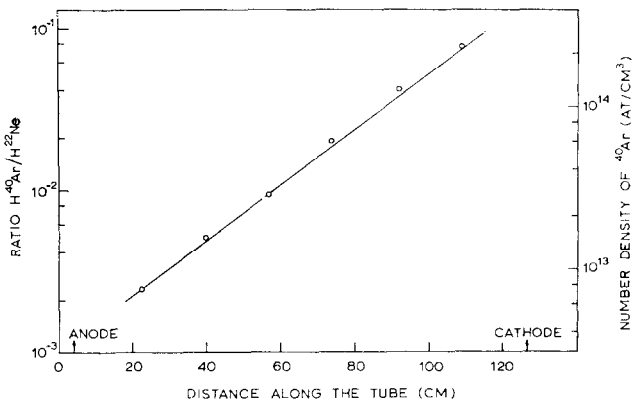

Fig. 4. An example of the cataphoresis in the stationary state in a mixture of neon with initially only 0.20% argon at a reduced total pressure of 3.32 torr and a tube current of 0.50 A. The ratio of the mass-spectrometrical peak heights of ^{22}Ne and ^{40}Ar is given as a function of the location in the discharge. The exponential relation is in good agreement with the theory. At the low percentage, only a fraction of all ions are argon ions.

b. The axial gradient of the argon as a function of the total gas pressure. In the case that all ions are argon ions ($\alpha = 1$), the gradient of the argon density $d/dx \, n_{Ar}$ is given by:

$$\frac{d}{dx} n_{Ar} = \frac{\mu_{Ar}^{+}}{D} \frac{1}{\mu^{-}} \frac{J}{e}. \tag{3}$$

The pressure dependence of the gradient $(d/dx)\ n_{Ar}$ reduces to the pressure dependence of $1/\mu^-$, if we bear in mind that the quotient μ_{Ar}^+/D does not depend on the pressure at a constant gas temperature. The electron mobility μ^- is inversely proportional to the gas density[10] (or the reduced pressure i.e. the pressure that would occur when the gas is brought to a temperature of 0°C at a constant gas density). Moreover, the electron mobility is a weak function of the electron temperature ($\approx 20.000°K$)[11]. With changing pressure the electron temperature will be influenced, and consequently the electron mobility too. In first approximation we may expect a proportional relation between the gradient $(d/dx)\ n_{Ar}$ and the reduced pressure.

Measurements of the argon gradient $(d/dx)\ n_{Ar}$ as a function of the reduced pressure were carried out in a mixture of neon with initially 1.07% argon (fig. 5). The relation between the gradient and the pressure is not exactly proportional. A slight deviation exists. The deviation of the proportional relation may be ascribed to the effect of the changing electron temperature on the electron mobility.
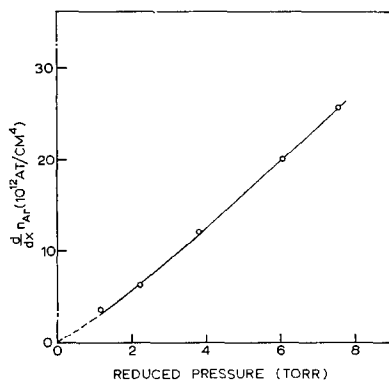

Fig. 5. The axial gradient of the argon density $(d/dx)\ n_{Ar}$, in a mixture of neon with initially 1.07% argon, as a function of the reduced pressure, at a tube current of 0.30 A and at an average gas temperature of 525°K.

c. The axial gradient of the argon as a function of the tube current. If we assume as gas mixture of neon with argon, in which nearly all ions are argon ions, e.g. neon with 1% argon, the gradient of the argon $(d/dx)\ n_{Ar}$ is given by formula (3). Keeping all parameters constant with the exception of the tube current by means of a furnace the gas temperature was kept constant the gradient $(d/dx)\ n_{Ar}$ will change proportionally with the tube current. However, with a changing tube current the electron temperature will change also by a small amount, and consequently, the electron mobility μ^- will to a small extent be influenced.

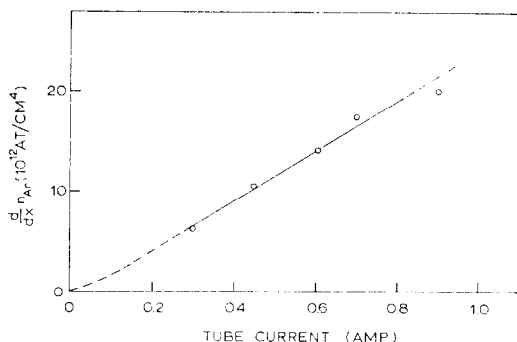Measurements of the argon gradient $(d/dx)\ n_{Ar}$ as a function of the tube

Fig. 6. The axial gradient of the argon density (d/dx) n_{Ar}, in a mixture of neon with 1.07% argon as a function of the tube current at a reduced total pressure of 2.18 torr and at an average gas temperature of 510°K.

current were carried out in a mixture of neon with initially 1.07% argon (fig. 6).

d. **The axial gradient of the argon as a function of the gas temperature.** If we assume a gas mixture of neon with argon, in which all ions are argon ions, e.g. neon with 1% argon, the axial gradient of the argon admixture is given by formula (3). Only the factor μ_{Ar}^-/D in formula (3) depends on the gas temperature[10][12] at constant density. In the gas temperature range under consideration, 300-600°K, the change in the electron temperature was very small and consequently the change in μ^- was
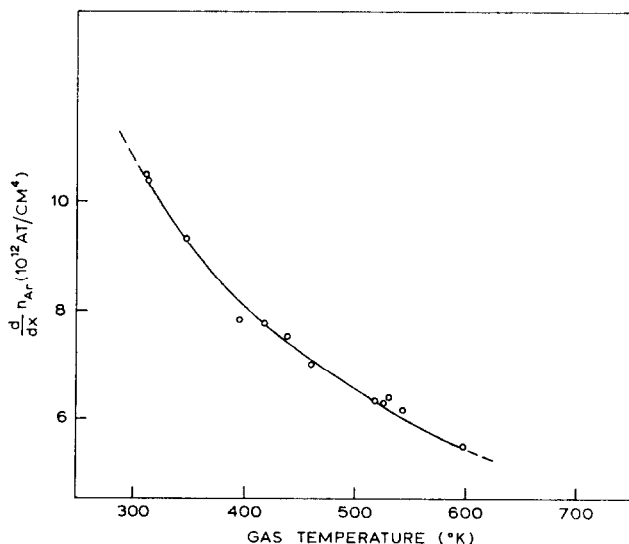

Fig. 7. The axial gradient of the argon density (d/dx) n_{Ar} in a mixture of neon with 1.07% argon as a function of the gas temperature at a reduced pressure of 2.18 torr and a tube current of 0.30 A.

small. With electric probes the electron temperature ($\approx 21.000°K$) was measured at different gas temperatures and no differences were observed[13]).

The gradient (d/dx) n_{Ar} was measured in a mixture of neon with initially 1.07% argon as a function of the gas temperature (fig. 7).

According to formula (3) the gas temperature dependence of (d/dx) n_{Ar} is equivalent to the gas temperature dependence of μ_{Ar}^{+}/D. In our experiments we found that (d/dx) n_{Ar} is almost proportional to $1/T$. Combination of this result with the temperature dependence of D[14]) will lead to the relative temperature dependence of the mobility of the Ar^{+}-ion in the gas mixture[2]).

3. *Experimental results in He–Ne*. *a*. Introduction. Cataphoresis can be used also as an experimental tool for the relative determination of the density n_a^{+} of the admixture ions as a function of any parameter. In a neon-argon mixture this would be the density of the argon ions. Here we are especially concerned with the density of the neon ions in a mixture of helium with a small amount of neon. The density n_a^{+} of the admixture ions is given by:

$$n_a^{+} = \frac{D}{\mu_a^{+}} \frac{1}{E} \frac{d}{dx} n_a, \tag{4}$$

compare formula (1). The quotient D/μ_a^{+} is a function of the gas temperature only. In our experiments with helium-neon, the gas temperature was kept constant, which could be realized by additional external heating of the discharge tube in a furnace. If the gradient (d/dx) n_a and the field strength E are measured as a function of the parameter under consideration, the density of the ions n_a^{+} can be determined relatively.

In the mixture He–Ne the density of the neon ions was determined as a function of the percentage of admixed neon and as function of the total gas pressure. This investigation led to information about the type of elementary collision processes in the He–Ne plasma. We shall not consider the density of the neon ions as a function of the tube current and the gas temperature (compared the mixture Ne–Ar), because we do not expect to give further qualitative information.

b. The axial gradient of the neon as a function of the percentage of admixed neon. The cataphoretic segregation in the stationary state was measured in a He–Ne plasma as a function of the percentage of neon, in the range of 0.05% to 4% neon. In this range the field strength varied from 11.5 to 9 volt/cm. In fig. 8 the gradient of the density of neon d/dx n_{Ne}, or (approximately) the density of the neon ions in arbitrary units, is given as a function of the percentage of admixed neon.

Even at a very low percentage of neon of 0.05 percent, the density of the neon ions is relatively high, about 17% of all ions are neon ions as could
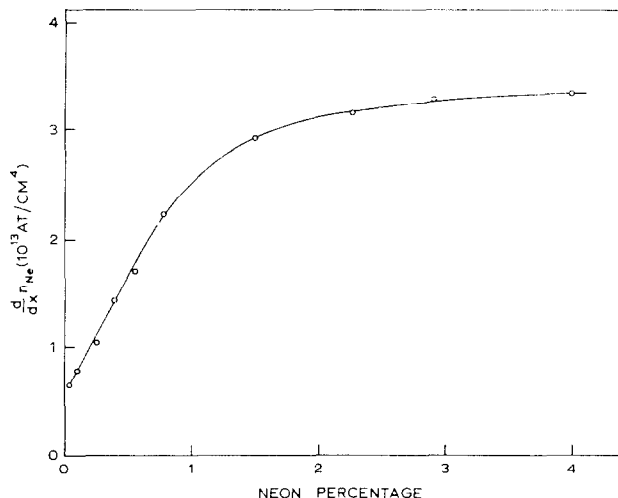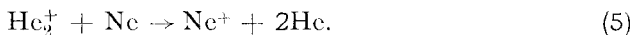
Fig. 8. The axial gradient of the neon density (d/dx) n_{Ne}, as a function of the local percentage admixed neon during the measurement in a helium-neon discharge. The reduced pressure is 4.55 torr, the tube current 0.5 A and the average gas temperature 550°K.

be verified[1]). An explanation of the very strong ionization of neon cannot be given on the basis of direct ionization by electron impact only. The Penning reaction via the helium metastable atoms is energetically impossible and charge exchange between a He^+-ion and a neon atom is energetically improbable. Another ionization mechanism must be responsible for the strong ionization. A proposed reaction[15]) is:

$$He_2^+ + Ne \rightarrow Ne^+ + 2He. \tag{5}$$

The energy of the helium molecular ion is equal to the ionization energy of the helium atom $(V_i = 24.58$ volt[9])) minus the dissociation energy of the helium molecular ion. In the literature several values for the dissociation energy of the helium molecular ion are given[16][17][18]) (ranging from 2.2 to 3.1 eV). The energy of the molecular helium ion must be near to, but larger than the ionization energy of the neon atoms $(V_i = 21.56$ volt[9])).

In a helium-neon plasma are other indications of a reaction as mentioned in (5):

Microwave experiments have been performed in the after-glow of a helium-neon plasma[15]). One needs the reaction (5) to explain the experimental results.

Even with traces neon in helium (percentages of neon much smaller than 0.05%, the He_2^+-ions will vanish[28]). When the percentage of neon is larger than, say 0.05%, the production of neon ions according to reaction (5) is limited by the production of the He_2^+-ions, as follows from fig. 8. For the

neon ion density (or the neon ion production) is not proportional to the neon density. Then the density of the ionizing particle He_2^+ must decrease strongly even at small percentages of neon.

In helium with 0.05 percent of neon, the main reason for ionization will be the process stated in reaction (5). With an increasing percentage of neon the ionization of neon by direct electron impact becomes more important. The production of ions by direct electron impact is proportional to the density (or percentage) of neon. When we suppose that the ionization contribution via the He_2^+-ion does not depend on the percentage of neon, then the two mechanisms of ionization will lead to the linear dependence of the neon ion density on the percentage neon (between 0.05 and about 0.8 percent, see left hand part of fig. 8).

For more than two percent of neon the density of the neon ions is nearly independent of the percentage of neon. This suggests a saturation of the neon ion density: nearly all ions are neon ions. A confirmation was obtained from cataphoresis measurements carried out in a triple mixture of helium with neon and argon[2]) (not described in this paper).

c. The axial gradient of the neon as a function of the gas pressure. Especially at very low percentages of neon, it was assumed that the neon is ionized in collisions with the helium molecular ions. The normal way of ionization by direct electron impact does not fit in this case,
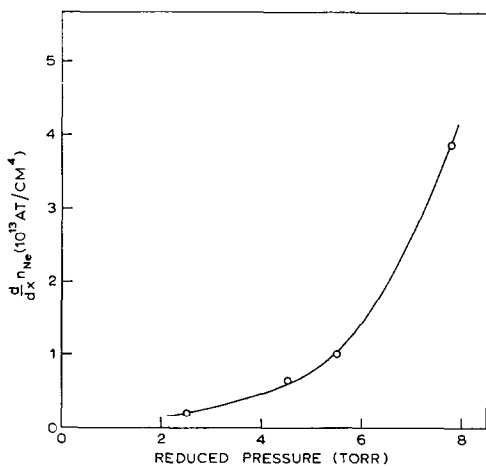

Fig. 9. The axial gradient of the neon density $(d/dx)\ n_{Ne}$ in a mixture of helium with 0.1% neon, as a function of the reduced total pressure, at a current of 0.50 A, and an average gas temperature of 640°K.
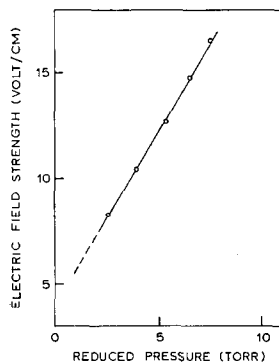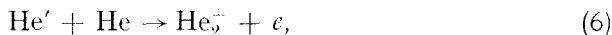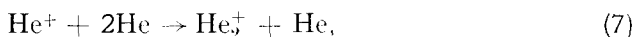
Fig. 10. The electric field strength in a discharge in helium with 0.1% neon as a function of the reduced total pressure; tube current 0.50 A. The average gas temperature was 640°K.

as the He_2-molecule in the ground state does not exist[18]. The production of the helium molecular ions occurs either according to the two particle collision process

$$He' + He \rightarrow He_2^- + e, \tag{6}$$

in which the highly excited helium atom He' associates with He in the ground state, or according to the three particle collision process:

$$He^+ + 2He \rightarrow He_2^+ + He, \tag{7}$$

in which the He^+-ion associates with one He, while the energy is carried away by the second He-atom. The two processes depend both on the total pressure and consequently the ion density (or cataphoresis) of the neon, at small neon concentrations, is pressure dependent too[21][22]).

The axial gradient of the density of the neon was measured in a helium-neon plasma (0.1% neon) as a function of the reduced total pressure (fig. 9). Moreover, the electric field strength was measured as a function of the reduced pressure (fig. 10).
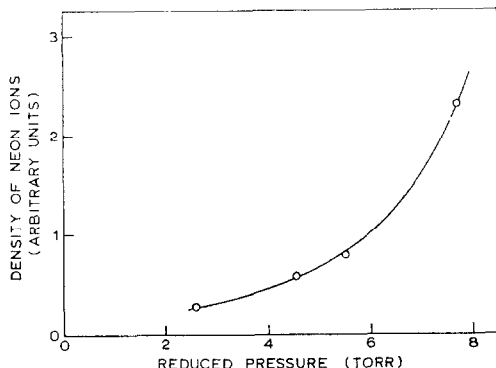

Fig. 11. The neon ion density in arbitrary units in a discharge in helium with 0.1% neon as a function of the reduced total pressure. The tube current was 0.50 A and the average gas temperature was 640°K.

The neon ion density as a function of the pressure was derived from fig. 9 and fig. 10 with the help of formula (4). The result is given in fig. 11. A pressure dependent neon ion density was found, which confirms the "occurrence" of reaction (5) and (6) or (7). The pressure dependence in the mixture He–Ne is more pronounced than that in the mixture Ne–Ar. This is caused by the fact that the formation of the ionizing particle He_2^+ is strongly pressure dependent.

d. Conclusions about the formation of the helium molecular ions. In the literature[21][23][24][25] several formation processes of helium molecular ions are mentioned. Two of them may be important in the helium-

neon plasma[25]), and are given in the reactions (6) and (7). In the active plasma in helium with 0.05% neon at a pressure of about 5 torr, a fraction (about 17%) of the ions are neon ions[2]). The other ions are helium ions. Oskam[15]) made measurements during the afterglow of a silmiar plasma. It appeared that the afterglow is controlled by the ambipolar diffusion of the Ne^+-ions.

At the moment that the discharge was switched off, about 83% of the ions were He^+-ions. (The density of the He_2^+-ions is low since they are destroyed by the neon atoms rapidly). During the afterglow measurements (more than 1 m s after switching off the discharge) the He^+-ions had disappeared. Recombination of the ions at the wall is impossible because of the small time interval of 1 ms. Therefore the He^+-ions disappeared in the volume. Volume recombination of the He^+-ions with electrons is very improbable (small recombination coefficient in the active plasma as well as in the afterglow)[26]). The three-particle process (7) will be responsible for the disappearance of the He^+-ions. The He_2^+-ions formed in the process (7) will disappear again in a collision with a neon atom. The three-particle collision process (7) will be an important process at pressures of about 5 torr. Since Oskam does not find He^+ in the afterglow of the helium-neon discharge, we may conclude that the cross sections for the processes (5) and (7) are large[27]).

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ERRATUM

On the formalism of lambda phase transitions

[Physica **34** (1967) 220]

by C. J. GORTER

1. The formulae on page 221 line 19 should be read:

$$C_H \propto -\{\Delta T \ln^3(\Delta T/\theta)\}^{-1} \quad \text{and} \quad \Delta M \propto \ln^{-2}(\Delta T/\theta),$$

2. the equations (4), (5), (6) and (8) should be:

$$\Delta S = -2A(\Delta T/\theta^2)\ln(\Delta T/\theta) - A\Delta T/\theta^2 \tag{4}$$

$$C = -2A(T/\theta^2)\ln(\Delta T/\theta) - 3AT/\theta^2 \tag{5}$$

$$\Delta G = -A(\Delta T/\theta)\ln^{-2}(\Delta T/\theta) \tag{6}$$

$$C = -2A(T/\theta\Delta T)\ln^{-3}(\Delta T/\theta) + 6A(T/\theta\Delta T)\ln^{-4}(\Delta T/\theta) \tag{8}$$

3. the end of the sentence on page 222 line 3 should be:

while the signs of (6), (7) and (8) have to be reversed.

The author is indebted to Mr. Th. J. Siskens, who called his attention to most of these corrections.