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1. INTRODUCTION.

Measurements of the mobility of ions in liquid He^3 have been performed only recently and in an incomplete way (1,2). The ionic mobility measured at the vapour pressure as well as under higher pressure are given in this article. Other measurements are in progress, so as to obtain experimental data at lower temperatures, but the values reported here give a sufficiently complete picture of the trend of mobilities over a wide range of temperatures and densities.

The interpretation of the data certainly needs an adequate theory of quantum fluids, and therefore it is understandable that every approximation attempted with classical simplified models is unsatisfactory.

Instead there is interest in the recent attempts of the Chicago group. The Rice-Allnatt theory (3) for transport phenomena in classical liquids, modified for quantum effects, has been used by Davis, Rice and Meyer (4) to calculate the mobility of positive ions in He^4 and He^3 . Such a theory will be compared with experimental results in the discussion of the present work.

In addition the same authors compute the mobility of negative ions under the hypothesis that they are free electrons, by using the transport theory of electrons in solids, with suitable simplifying assumptions. This theory too will be compared with experimental data and discussed in the last section, but even now we may say that these two approaches may without

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doubt be considered to be good first approximations.

A very recent article by Clark⁽⁵⁾ looks especially interesting with regard to the interpretation of ionic mobility in He^3 , because for the first time the statistics of the particles of the fluid appears in it.

It is impossible to test this theory with the data presented here, because it predicts a dependence $\mu \propto (1/KT)^2$ only for temperatures much lower than those of our data. The extension of measurements to very low temperatures which we plan to do in the near future is then of great interest.

2. EXPERIMENTAL APPARATUS.

The cell and the method of measurement are the same as described in Ref.(1).

To carry out the measurements under pressure the system shown schematically in Fig. 1, was constructed. It is

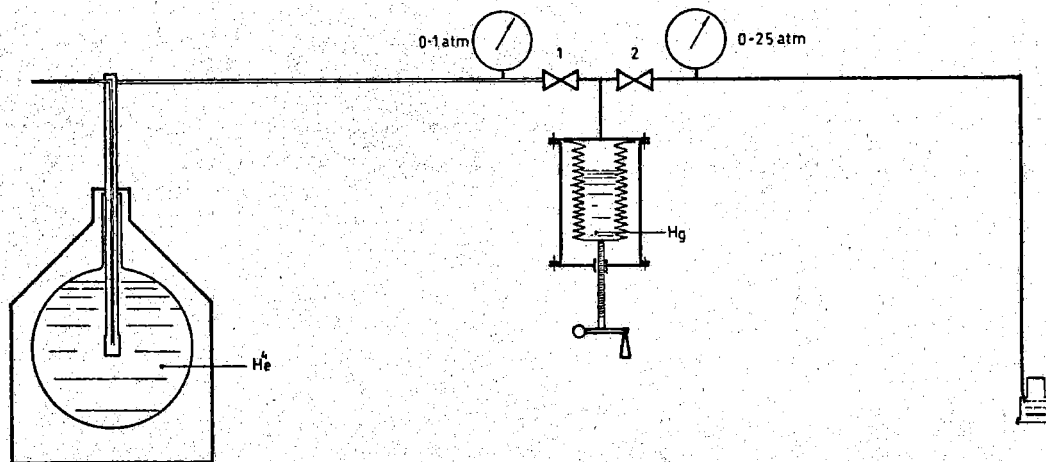


FIG. 1 - He^3 pressurizer up to 20 Atm. After passing through a trap at 4.2°K , He^3 is compressed in the cell in successive cycles by means of a stainless steel Toepler pump and valves 1 and 2. One cycle permits to achieve ~ 6 Atm.

essentially a stainless steel Toepler pump. He^3 , after passing through a purifier at 4.2°K and 1Atm, goes into a steel bellows which has a working volume of $\sim 150 \text{ cm}^3$ (since the bellows has a maximum contraction which is only a part of the total length, it was filled for $\sim 4/5$ of its volume with Hg in order to obtain practically no residual volume). The dead space is the capillary tube (to the right of valve 1) which connects the bellows to the cell, and the manometer (4 to 5 cm^3).

The experimental data shown in Figs. 2-6 are the mean value of at least three measurements of mobility with different electric fields between 180 and 430 V/cm. As already quoted in Ref.1 for such values of electric field, the mobility is practically field independent.

The errors given in the Figures are obtained by estimating the accidental errors affecting the measurements, and not taking into account the systematic ones which could influence the absolute values of the measurements, and which are much more difficult to estimate.

The temperature, in the range covered by the He³ refrigerator, was measured by means of a previously calibrated carbon resistor.

3. RESULTS.

The values of the mobility for ions of both signs, with the liquid under its own vapour pressure, are shown in Fig. 2.

Actually the measurements were performed at a pressure of 1 to 2 cm Hg above the vapour pressure to avoid the presence of bubbles.

In Fig. 3-6 are shown the mobilities vs. temperature and density for the two kinds of ions. The two families, $\mu(T)$ for $\rho = \text{const.}$ and $\mu(\rho)$ for $T = \text{const.}$, are plotted.

It appears from these curves that the experimental results for the positive ions give rise to no uncertainties, while for the negative ions the behaviour is quite different.

In Fig. 5 the points for temperatures above 2°K are very close together and often overlapped within the limit of errors. Therefore the behaviour of the curves plotted is to a certain extent arbitrary, and the actual behaviour may be slightly different.

Only the three smoothest curves are plotted in Fig. 6.

The values reported in Ref. 2, which can be compared with ours, are in good agreement. A systematic difference of less than 10% may be noted, which is no doubt due to a small difference in the calibration of the two experimental set-ups.

4. DISCUSSION.

The interpretation of the experimental data is still unsatisfactory at present. For this reason, it isn't unreasonable to briefly consider even the classical models, just to

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state the limits of the approximation.

The classical theories may be summarized in the formulas due to Einstein

$$(1) \quad \mu = (eD/kT)$$

and to Stokes-Einstein

$$(2) \quad D = (kT/6\pi\eta r)$$

Combination of (1) and (2) leads to the well known Walden's rule

$$(3) \quad \eta\mu = \text{const}$$

where the constant contains the ionic radius.

The values of $\eta\mu$ in arbitrary units, calculated from the values of μ at vapour pressures, are shown in Tab. I for both positive and negative ions at different temperatures.

TABLE I

$\eta\mu$ product for positive and negative ions computed from experimental values of μ at vapour pressure and from the viscosity measurements by Zinovi'eva⁽⁶⁾

T	$\mu_+ \eta$	$\mu_- \eta$
2,6	15,6	4,91
1,98	-	5,79
1,68	16,1	-
1,46	16,2	6,24
1,10	-	6,87
1,08	17,3	-
0,86	18,85	-
0,83	-	7,33
0,72	-	7,56
0,39	> 25	-

From Tab. I one may note that Eq. 3 is satisfied only for positive ions and only for temperatures above $\sim 1.4^\circ\text{K}$. In the classical representation, this fact may be explained as due to the constancy of the ionic radius at high temperatures, while for the negative ion the behaviour could exhibit a dependence of the ionic radius on $1/T$, but probably it indicates instead the inadequacy of this model for the negative ions.

The lack of data for the values of n under pressure doesn't allow us to compute the product $n\mu$ for values of μ measured for densities higher than those at vapour pressure.

This could give information about the variation of the radius of the ion with pressure.

Another quantity which can be calculated in the approximation of this model is the diffusion coefficient of the ion, from Eq. 1.

The diffusion coefficient for positive ions is shown in Fig. 7 together with the self diffusion coefficient for He^3 , as measured by Hart & Wheatley⁽⁷⁾.

Neglecting the absolute values (D_{i+} is about $1/7 D_{\text{He}^3}$), one may notice that the dependence on the temperature is the same for the two curves down to $1.2 \pm 1.4^\circ\text{K}$, i.e., the value found previously for the limit of validity of this model.

A remarkable attempt has been made by Davis, Rice and Meyer⁽⁴⁾ to explain the behaviour of the ions of both signs in liquid He^3 and He^4 .

For the positive ions they use an extension of the Rice-Allnatt⁽³⁾ theory for transport phenomena in classical liquids. The extrapolation to quantum fluids is essentially done by replacing the thermodynamic temperature with a quantum temperature τ_Q , following an idea by Mazo & Kirkwood⁽⁸⁾ who show that quantum effects may be absorbed in this parameter τ_Q .

The mobility of positive ions is given in this theory by

$$(4) \quad \mu_+ = e / (\zeta_H + \zeta)$$

where

$$(5) \quad \zeta_H = \frac{8}{3} \rho_N \sigma_i^2 g_2(\sigma_i) \frac{2\pi m_i m k \tau_Q}{m_i + m}$$

and

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$$(6) \quad \zeta = (4\pi m^2 c^3 \rho_m)^{-1} \left[\frac{1}{3} \rho_m \int_{\sigma_i}^{\infty} \nabla^2 V(R) g_2(R) dR \right]^2$$

with e the electron charge, ρ_N and ρ_m are the number and the mass density, respectively, c is the sound velocity, $V(R)$ the Lennard-Jones potential plus a shielded Coulomb field, m is the atomic mass of He^3 , σ_i the contact diameter between ion and neutral atom, m_i is the mass of the ion and $g_2(R)$ the 'radial' distribution function. The latter is composed by two parts

$$g_2(R) = g_0(R) + g_p(R),$$

where $g_0(R)$ is the unperturbed distribution function generated by the Lennard-Jones potential, and $g_p(R)$ is the correction associated with the electrostrictive forces due to the charge on the ion, following the model given by Atkins⁽⁹⁾. The positive ion is assumed to be He^2 and hence $m_i = 2m$.

In Ref.(4) the authors don't show any comparison between the observed mobilities for positive ions in He^3 and the values that can be computed from Eq. 4.

To test the theory we first calculated the term ζ_H for He^3 at a temperature of 2°K .

All the quantities appearing in Eq. 5 are easy to calculate. The values we used are at $T = 2^\circ\text{K}$, $\rho_N = 1.56 \times 10^{22}$, $\sigma_i = 2.7 \times 10^{-8}$, $\epsilon = 1.026$.

We computed τ_0 for He^3 by using the formulas and tables given by Kirkwood et al.^(8,10), obtaining a value of 11.0°K . The temperature dependence of is very small.

The value obtained for ζ_H is 2.4×10^{-10} g/sec which by itself would give a mobility lower by an order of magnitude than the observed one.

The addition of ζ , which is at least of the same order as ζ_H , would set the computed values farther apart from the observed ones. The agreement found by Davis et al.⁽⁴⁾ for He^4 then appears to be really fortuitous as they suspected.

The need for a quite different theory for the negative ions led Davis, Rice and Meyer⁽⁴⁾ to compute the mobility of the ions of this sign by starting from the hypothesis that they are free electrons.

Such an hypothesis appears to be reasonably true. The arguments presented by Atkins⁽⁹⁾ (and also by Kuper⁽¹¹⁾) in the case of He^4 , appear to us to be true for He^3 also.

In short, Atkins says that if the negative ion is a molecular system (like He_2) of helium or impurities (a much

less probable case), the electrostrictive forces won't be very different from those existing in the case of the positive ion and hence the mobility for ions of both signs will be very similar.

The marked difference between the experimental curves for He³ (Figs. 2,3,4,5) supports the validity of this argument perhaps even more than in the case of He⁴.

Davis et al. (4) compute the mobility of the negative ions by approximating the electron with a plane wave scattered by a suitable potential. The resulting expression for the mobility is

$$(7) \quad \mu_- = \frac{e \hbar^4 \beta^{1/2} a^2}{24 \sqrt{2} \pi^{3/2} m^*{}^{5/2} \rho_N^2 K_L C^2 k \tau_Q}$$

with $\beta = 1/KT$, a is the atomic diameter, K_L is the isothermal compressibility, m^* is the effective mass of the electron, $C = \frac{1}{2} \alpha [(\epsilon+2)/2\epsilon]^2 e^2$ where α is the atomic polarizability and ϵ is the relative dielectric constant.

Eq. 7 appears in Ref. (4) in this form in a note added in proof although in the text it doesn't contain τ_Q but only T .

The weakest point of this theory appears to be the way in which m^* is to be calculated. Indeed the authors, in order to evaluate m^* , follow a one to one correspondence with the polaron model (12,13).

So to calculate the frequency ω (the natural frequency of the lattice) which appears in the formula for the effective mass (13)

$$(8) \quad \frac{m^*}{m_e} = 1 + 0,02 \left[\frac{1}{2} (\epsilon_\omega^{-1} - \epsilon^{-1}) \frac{e^2}{\hbar} \left(\frac{2m_e}{\hbar \omega} \right)^{1/2} \right]^4$$

where

$$(9) \quad \omega = k \theta / \hbar \quad \text{and} \quad \theta = T \left(\frac{464}{C v} \right)^{1/3}$$

they approximate liquid helium with a Debye solid, justified with an observation about specific heat.

But the T^3 proportionality of the specific heat is valid only for He⁴ II, and the situation with regard to He³ is even worse. The fact that the polaron model for m^* is inconsistent may be seen rather easily from the temperature dependence of m^* .

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Indeed, assuming Eq. 7 is valid, and calculating from it the values of m^* by insertion of experimental values for μ_- , we obtain Tab. II from which it is easy to see that the dependence of m^* on T is, to a good approximation, of the form $\propto T^{-1/2}$.

The temperature dependence of m^* from Eq. 8 is roughly $\propto T^{-2}$.

We think then a more adequate calculation of m^* , taking into account the experimental results, is necessary for a proper formulation of this theory.

TABLE II.

Effective masses of electrons calculated by Eq.7 from the experimental values of μ_- here quoted

T	μ_- (cm ² /v. sec)	m^*/m_e
1,98	3,08.10 ⁻²	53
1,46	3,12 "	63
1,10	3,08 "	69
0,84	2,83 "	79
0,72	2,72 "	83

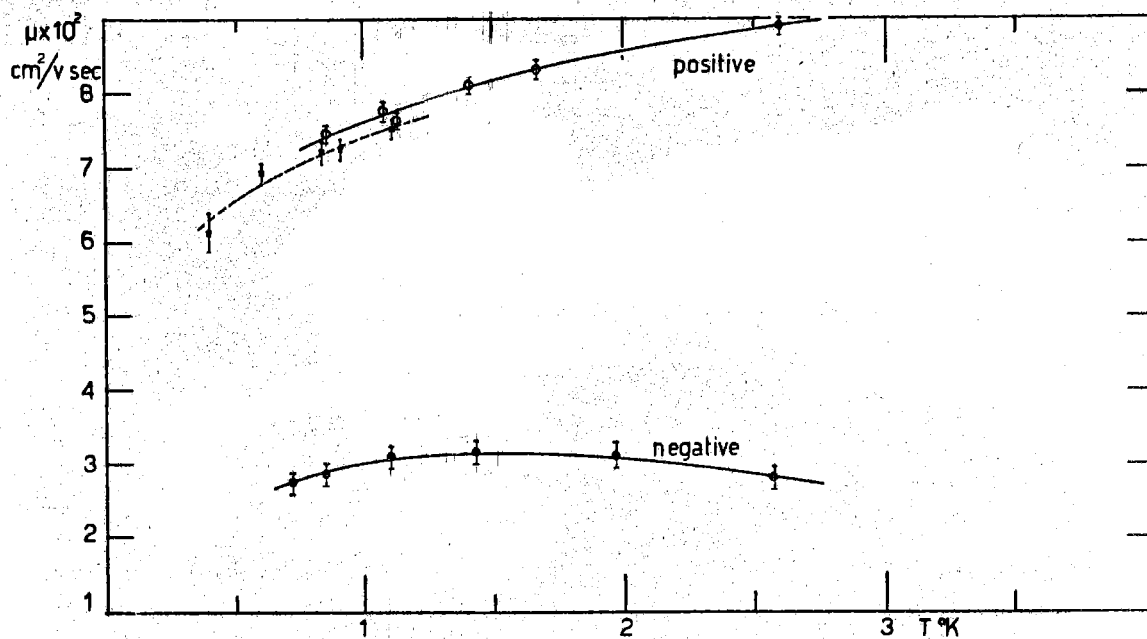


FIG. 2 - Mobility of charged particles of both signs at vapour pressure vs. temperature. The dotted line is an isobar at 0.5 Atm from which it is possible to extrapolate the behaviour at vapour pressure for temperatures down to 0.39°K.

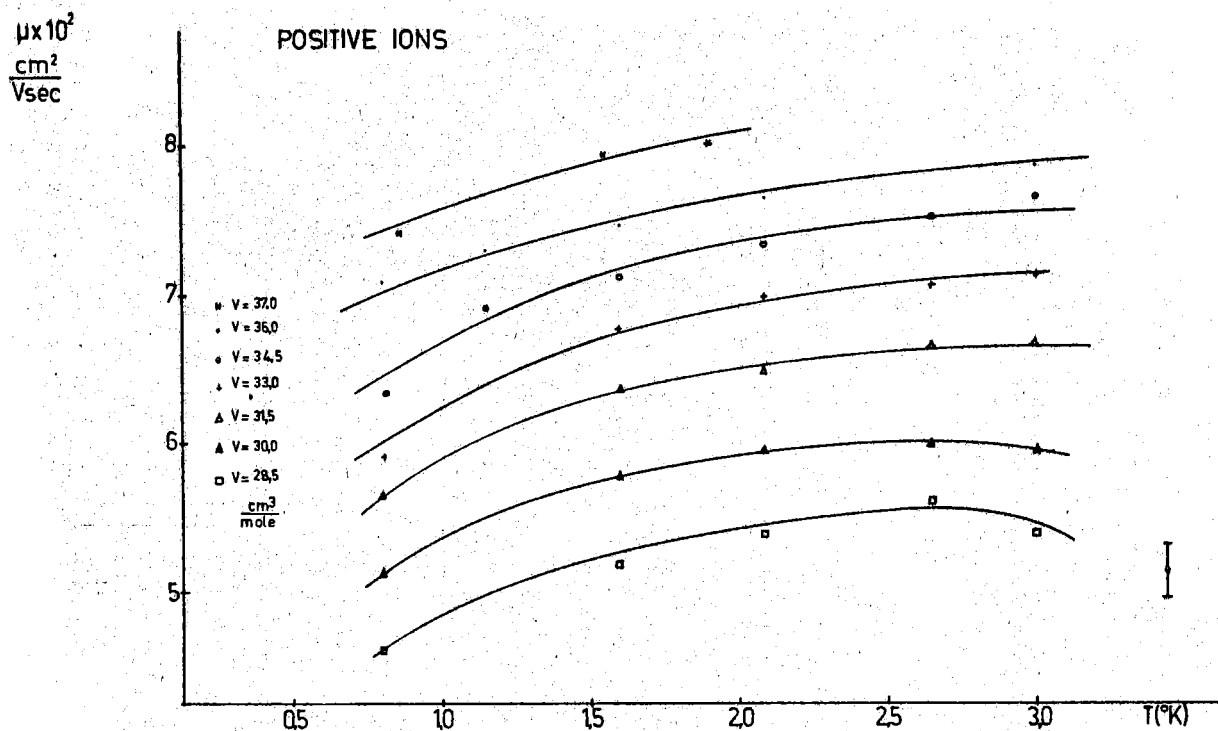


FIG. 3 - Positive ion mobility for several constant densities vs. temperature. Specific volumes are given at which measurements were made.

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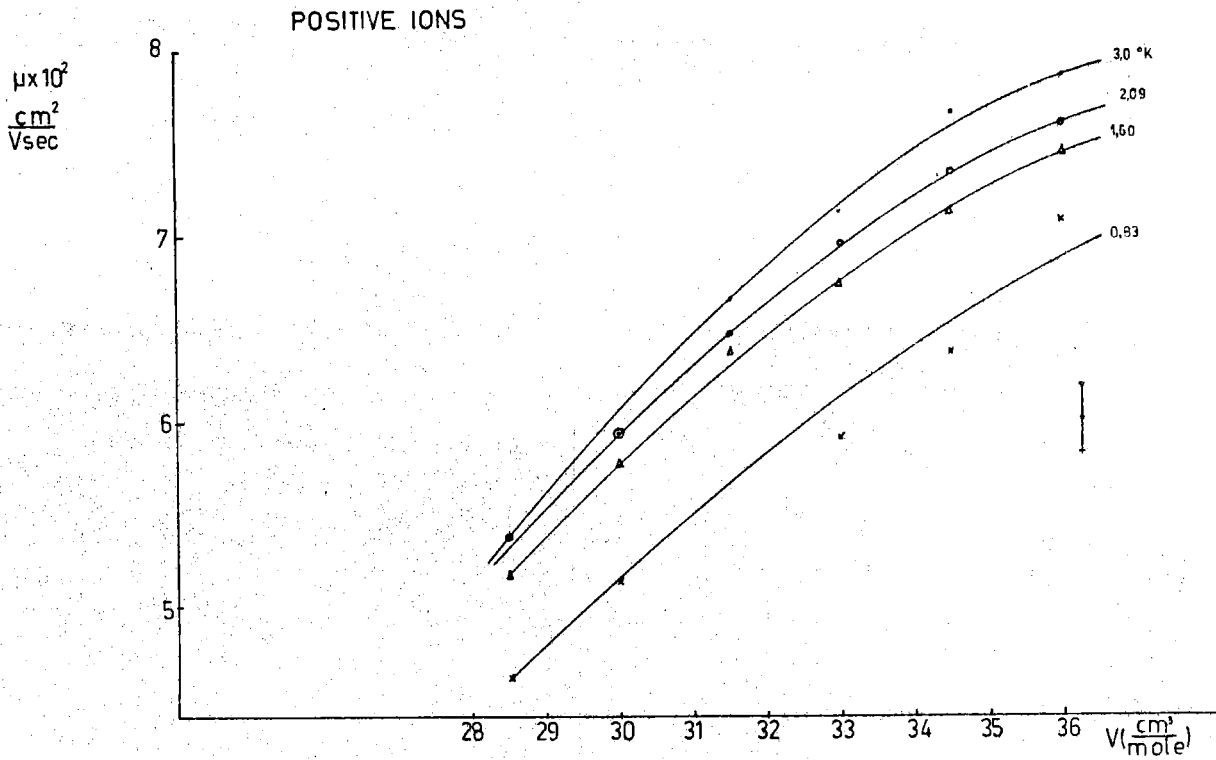


FIG. 4 - Positive ion mobility at different constant temperatures vs. specific volume.

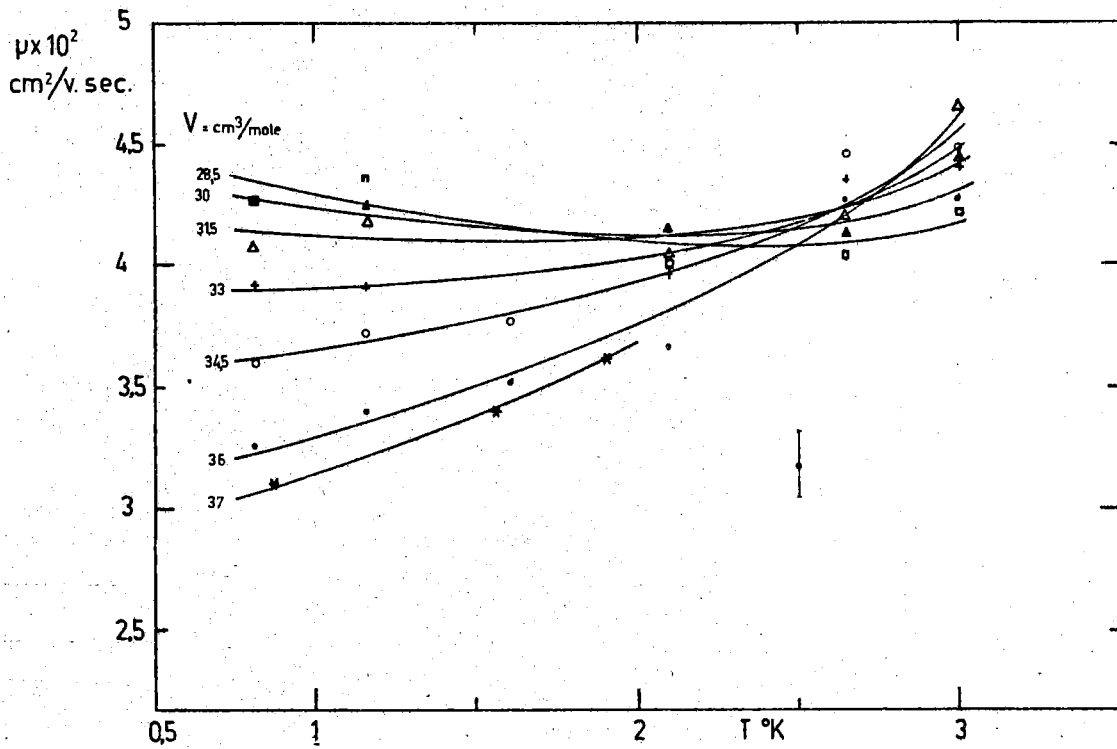


FIG. 5 - Negative ion mobility for the same densities as in Fig. 3 as function of temperature. As mentioned in the text the behaviour in the region above 2°K is rather difficult to determine without uncertainties.

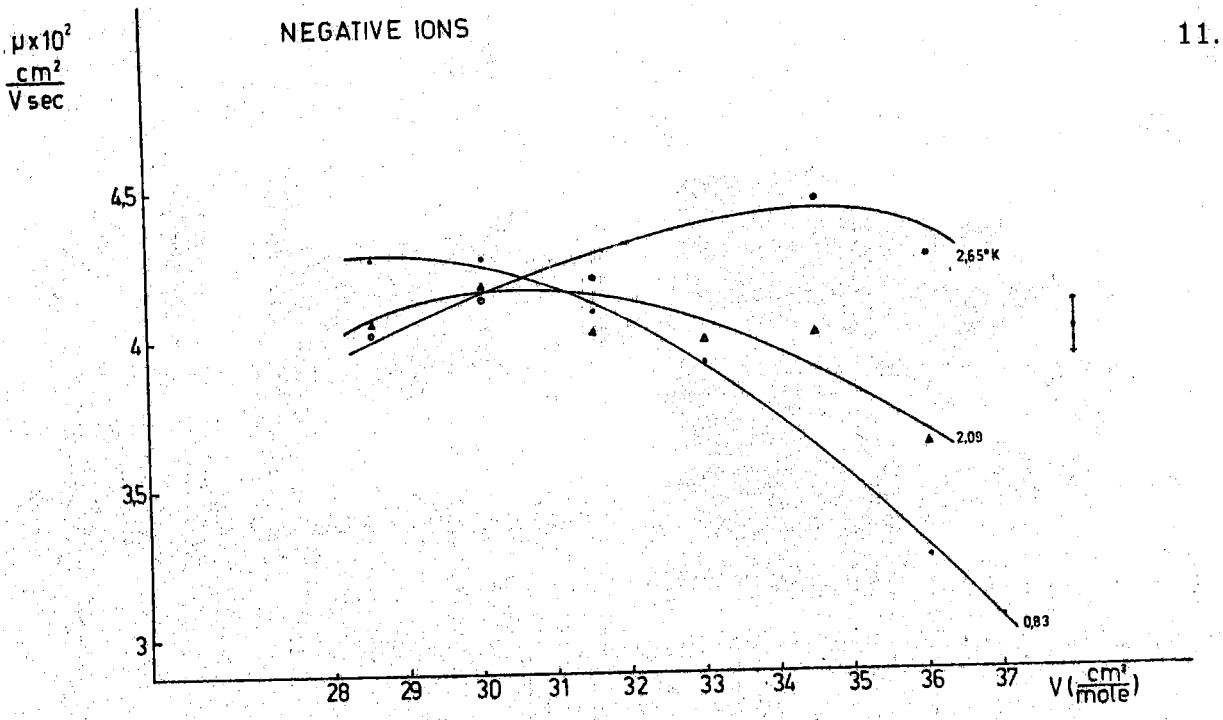


FIG. 6 - Negative ion mobility for three different temperatures as a function of specific volume.

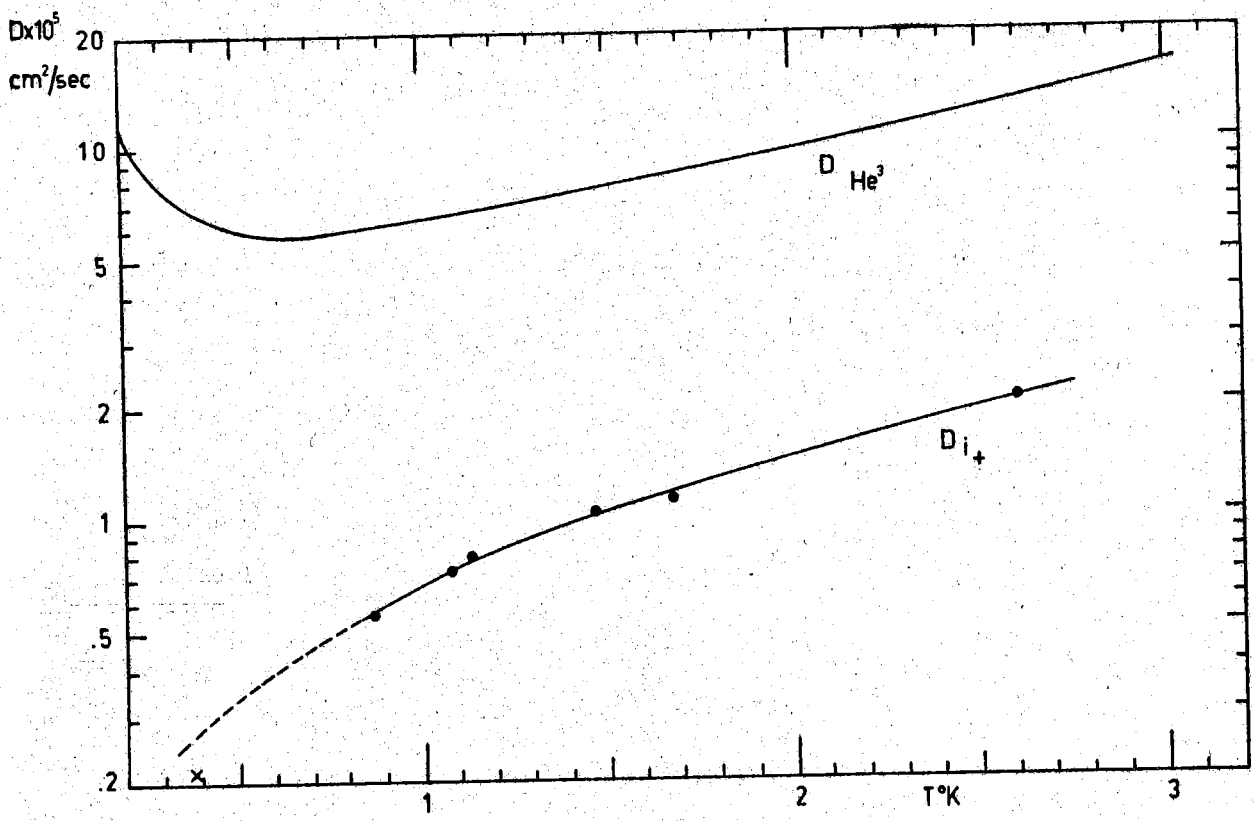


FIG. 7 - The figure shows a comparison between the diffusion coefficient of positive ions deduced from the Einstein relation $D_{i+} = KT\mu/e$. D_{He^3} is the autodiffusion coefficient measured by Hart and Wheatley⁽⁷⁾. The point x is calculated from the 0.5 Atm data, and the dotted line is a reasonable extrapolation based on this point which allows us to deduce the absence of a minimum corresponding to that appearing in the D_{He^3} curve, in the D_{i+} curve.

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