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Transmission of negative ions through the liquid–vapour surface in neon[†]

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Abstract. Experiments on the transmission of negative ions from liquid neon to the vapour have been performed at various temperatures and at various liquid levels. The results show that the barrier is due to the dielectric discontinuity. The Smoluchowski equation gives a good description of the results, provided that we use for the electric field E the values of the field E_L which exists at the liquid side of the interface.

1. Introduction

We report in this paper some results on transmission of negative ions from liquid neon into the vapour. Transmission experiments have been extensively performed for ^{4}He below the lambda point. The difficulty that the ions have in passing through the liquid–vapour interface has been explained by the existence of a small potential barrier, which is due to the dielectric discontinuity (Bruschi *et al* 1966, Rayfield *et al* 1971).

The dependence of the surface trapping time τ on temperature and electric field has been described at first in terms of brownian diffusion over the barrier (Schoepe and Rayfield 1971). The difficulties which resulted from this description seem to be partly overcome in a tunnelling model developed recently by the same authors (Schoepe and Rayfield 1973).

We think it is useful at the present stage of understanding to carry out experiments on liquids other than ^{4}He, in order to get a considerable variation in the physical properties which are relevant for the transmission. Excess electrons injected into liquid neon are localized in a bubble, as are excess electrons in liquid helium (Bruschi *et al* 1972, Loveland *et al* 1972). The dielectric constant, the temperature and the electric field involved, are greater in the case of neon, while the mobility of ions is lower. With a curvature at the top of the barrier not very different in the two cases, the trapping time τ at the neon interface would be very low. On the contrary, the first observations suggested that the trapping times were much greater than expected. We have therefore undertaken quantitative experiments.

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2. The experimental apparatus

2.1. *Cryogenics*

The cryostat is the same as that used in the measurement of the mobility in liquid neon, and is drawn in figure 1*a*. The brass experimental chamber can work at pressures up to 30 atm. It is suspended inside an exchange chamber which can be evacuated or filled with helium gas at low pressure. The outside bath is at a temperature of 4·2 K, which is well below the triple point of neon ($T \simeq 24$ K). The stainless steel capillary which connects the cell with the neon pressure system must therefore be placed inside an evacuated jacket and heated to prevent solidification. The temperature is regulated with standard electronics through the heater HT and monitored by a 1000 Ω Allen Bradley carbon resistor. The value of the temperature is deduced from the measurement of the liquid neon vapour pressure.

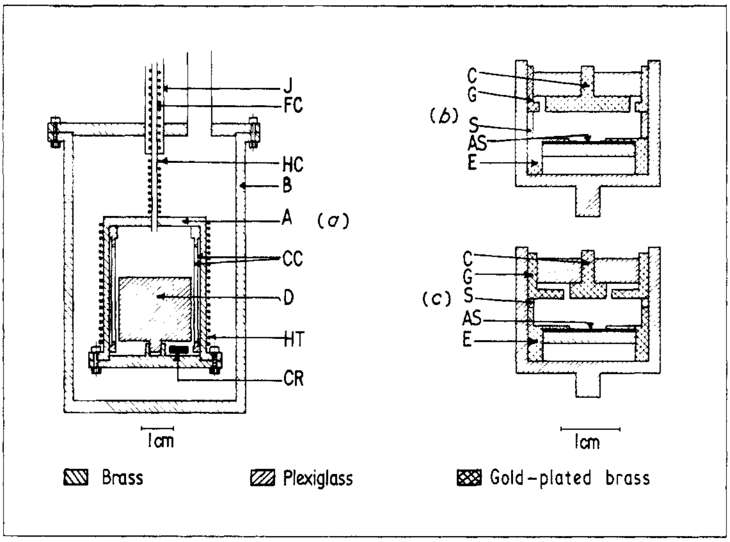

Figure 1. (*a*) Schematic view of the cryostat. A, experimental cell; B, exchange chamber; D, diode; FC, filling capillary; J, vacuum jacket; HC, capillary heater; HT, thermo-regulating heater; CR, carbon resistor; CC, cylindrical condenser.
(*b*) and (*c*) Two diode geometries. C, collector electrode; G, guard electrode; E, emitter electrode; AS, americium source; S, spacer.

2.2. *The measurement of the liquid level*

From the measurement of the capacitance C_x of the cylindrical condenser CC (figure 1*a*), we can deduce the position of the interface between the source and collector electrodes. The capacitance C_x is given by

$$C_x = C_p + C_0\varepsilon_V + (\varepsilon_L - \varepsilon_V)\, C_0(x/h) \tag{1}$$

where C_p is a stray capacitance which does not depend on the level, C_0 is the capacitance of the condenser, of height h, accessible to neon, x is the liquid level, ε_L and ε_V are the dielectric constants of the liquid and the vapour. The dielectric constant of neon has been calculated with the Clausius–Mossotti formula, using for the atomic polarizability the value $\alpha_0 = 3{\cdot}92 \times 10^{-25}\,\mathrm{cm}^3$ (Cook 1961). For the liquid it ranges from about 1·19 at 25 K to about 1·07 at the critical point.

The capacitances C_p and C_0 can be determined by measuring the capacitance C when the condenser is in vacuum and when it is filled with liquid neon. The vacuum capacitance $(C_p + C_0)$ changes only slightly with temperature, about 0·2% from 77 K to 20 K. The difference between the liquid level in the capacitor and in the diode can be calculated using values of the surface tension obtained from a corresponding states equation (Frisch and Salsburg 1968). The maximum difference in height is about 0·1 cm at $T = 25\,\mathrm{K}$.

2.3. *The experimental cell*

The experimental cell is a diode, 2 cm in diameter, contained in a plexiglass cylinder. The gap between the emitting and collecting electrodes is fixed at 0·5 cm. The electrodes are in a horizontal position, and the emitter is at the bottom. The ions are generated by a 400 μCi radioactive americium source (Radiochemical Centre, Amersham, England), which emits α particles at 5·6 MeV, and γ rays of 60 keV. We have used two different geometries, as shown in figure 1*b*, *c*. In the cell of the first type the guard collector has a negligible collecting area. It merely prevents spurious results, which can be due to a leakage current through the lateral insulating ring. In the second type of cell the emitter electrode is cup-shaped, and the central collector has the same area as the radioactive source.

3. The measurement of the trapping time

If J is the current density and σ is the surface charge density at the interface, the mean trapping time τ is given by the relationship

$$\tau = (\sigma/J) = (\sigma S/I) \tag{2}$$

where I is the total collected current, and S is the effective emitting area of the interface. The electric fields near the interface, E_L at the liquid side and E_V at the vapour side, are related to σ by the equation

$$\varepsilon_V E_V - \varepsilon_L E_L = 4\pi\sigma. \tag{3}$$

In the ohmic régime E_V and E_L are constant in space, and so the applied potential difference V_0 will be given by

$$V_0 = E_L t + E_V(d - t) \tag{4}$$

where t is the liquid thickness and d is the emitter–collector distance. Combining the equations (2), (3) and (4) we get

$$\tau = \frac{S\varepsilon_V}{4\pi(d - t)I}\left[V_0 - E_L(t + (d - t)(\varepsilon_L/\varepsilon_V))\right]. \tag{5}$$

The ohmic régime is certainly satisfied in the vapour because the negative carrier mobility is rather high, of the order of 100 or $1000\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. In the liquid, on the other hand, the mobility is low, between 10^{-3} and $10^{-2}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. Space charge effects may in general be present and therefore the equation (4) would be modified. Space charge effects have indeed been observed in the liquid when using a tritium source, but with the americium source the collector current was linear on the applied potential V_0, within 5%, from 5 up to 200 V. This fact can probably be explained as a combined result of both α and γ ionizations. Anyhow, it is easy to show that if the current is a linear function of the applied potential, the electric field must be constant in space.

We therefore make the assumption that in our experiments the electric field is substantially constant in the liquid, and we use equation (5) to compute the trapping time τ from the measured quantities. These are the liquid thickness t, the applied potential V_0, and the current I, which in turn determines the electric field E_L in the liquid phase through the measured I–V liquid characteristic.

4. Experimental results and discussion

A typical set of results, obtained at $T = 35{\cdot}7$ K, is shown in figure 2. The current in the vapour is measured while keeping the liquid level below the source electrode. The current reaches high values, of the order of 800 pA, with low electric fields.

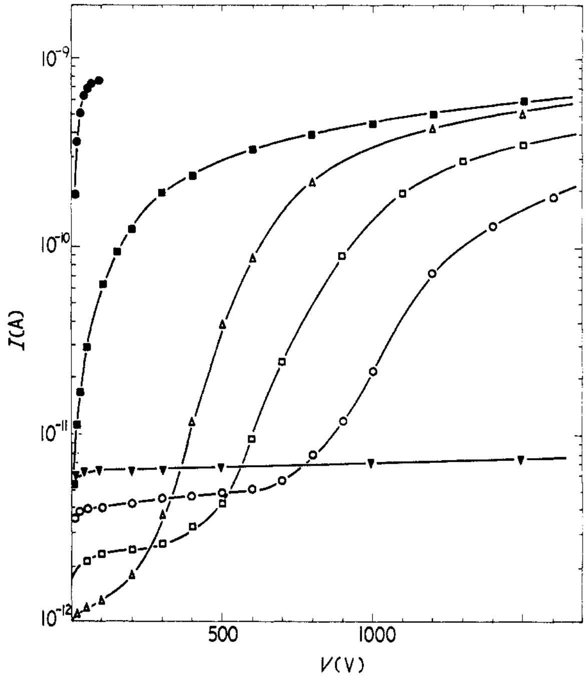

Figure 2. Some current–voltage characteristics obtained at $T = 35{\cdot}7$ K. (*a*) Interface between the electrodes at various liquid thickness t: △ $t = 0{\cdot}37$ cm, □ $t = 0{\cdot}26$ cm, ○ $t = 0{\cdot}15$ cm, ▼ $t = 0{\cdot}10$ cm; (*b*) full vapour ●; (*c*) full liquid ■.

When the liquid level is just above the source the current is drastically reduced by about two orders of magnitude. Moreover it is practically field-independent over a large range of electric fields. We refer to this current as the 'plateau' current. If the level is raised once more, one obtains a shorter plateau region followed by a region where the current grows rapidly with the applied potential. From figure 2 we see that the current–voltage characteristic depends on the interface level, approaching the liquid characteristic as the level approaches the collector.

4.1. The plateau region

The reduction in current when the level is placed between the electrodes shows that the electric field in the liquid is reduced. While this fact can be easily explained with the existence of a trapped charge layer at the interface, the plateau current cannot be explained by a surface effect. In this region, indeed, the current I, and so the electric field in the liquid E_L, are nearly constant. Therefore, if this is a surface effect described by equation (5), it should be controlled by a trapping time τ increasing with the applied potential V_0. This result has no 'physical sense', and thus the carriers of the plateau current must be generated above the liquid–vapour interface. We can indeed explain the plateau if we take into account the ionization in the vapour produced by the γ rays of the americium source. Because the mobility of electrons in the vapour is very high, the current will saturate to a constant value at low electric fields. Let us assume that the radioactive source is an isotropic point source and that the number of ions is proportional to the number of photons and to their path λ in the vapour. The chamber is a cylinder of radius R and therefore the number of ions dN, produced inside the solid angle dΩ and in a time dt, will be

$$\mathrm{d}N \propto \lambda\,\mathrm{d}\Omega = [(d-t)/\cos\theta]\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}t \qquad \text{for} \quad 0 \leqslant \theta \leqslant \beta_1$$

and

$$\mathrm{d}N \propto \lambda\,\mathrm{d}\Omega = \left[\frac{R}{\sin\theta} - \frac{t}{\cos\theta}\right]\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}t \qquad \text{for} \quad \beta_1 \leqslant \theta \leqslant \beta_2$$

where θ and ϕ are the polar coordinates, and the angles β_1 and β_2 are those shown in figure 3.

Integrating the above equations over the whole volume occupied by the vapour yields for the saturated plateau current

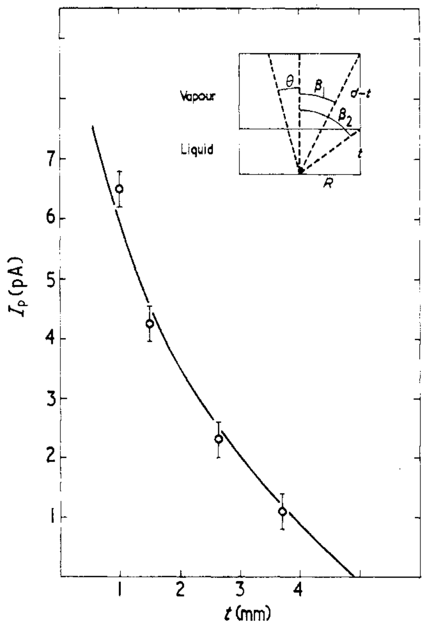

Figure 3. The plateau current I_p as a function of the liquid thickness t.

$$I_p = a\left[R\beta_2(t) + t\ln\frac{t}{(R^2+t^2)^{1/2}} - b\right] \tag{6}$$

where $b = -R\beta_1 - d\ln d/(R^2 + d^2)^{1/2}$, and a is a constant which depends on the intensity of the source, the ionization cross section, and the density of the vapour.

The values of the plateau current, measured at $T = 35{\cdot}7$ K for some values of the level t, are reported in figure 3. The full curve is the function $I_p(t)$ given by the relationship (6). The constant a has been adjusted to fit the experimental points. The dependence on the level is in good agreement with the experimental results, and therefore we conclude that the plateau current is due to γ ionization in the vapour. In the study of the surface effects, this plateau current will be subtracted from the total current.

4.2. The liquid–vapour barrier

The potential energy of a point charge e, placed in the liquid at a distance x from the liquid–vapour interface is given by

$$\Phi(x) = \frac{e^2(\varepsilon_L - \varepsilon_V)}{4\varepsilon_L(\varepsilon_L + \varepsilon_V)x} = \frac{A}{x}. \tag{7}$$

The dependence of the constant A on temperature is shown in figure 4. The expression (7) is valid only for a point charge and for a sharp transition from liquid to vapour. In this case we would have an infinite barrier. But actually the density of the fluid changes smoothly from the liquid to the vapour density over a distance of the order of 10 Å. Moreover our charge is localized in a bubble with a radius of about 10 Å. Therefore the relationship (7) is not valid when the ion is very near the transition region. We should expect that the actual barrier is finite, with a maximum Φ_0 at a distance x_0 from the interface of the order of few Å.

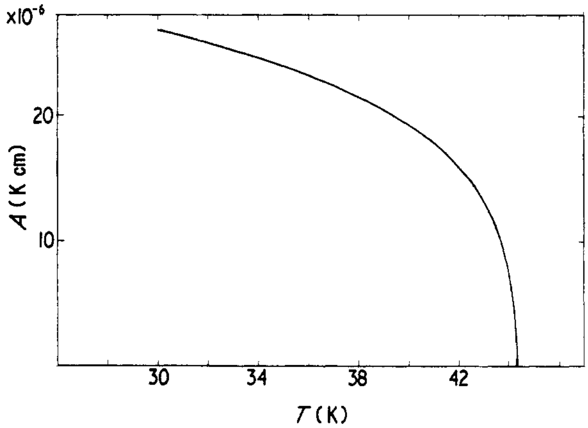

Figure 4. The constant A of the image potential for neon as a function of temperature.

If a homogeneous electric field E is applied normally to the interface, the total potential energy function becomes

$$\Phi(x) = (A/x) + eEx. \tag{8}$$

This function has a minimum at $x_m = (A/eE)^{1/2}$, with a value $\Phi_m = 2(eEA)^{1/2}$, and the barrier height for the ion is therefore $\Delta\Phi = \Phi_0 - \Phi_m$.

The value of x_m depends on the temperature through A, and on the electric field E. As an example we find $x_m = 147$ Å at $T = 35{\cdot}7$ K and $E = 1000\,\mathrm{V\,cm^{-1}}$. The function $\Phi(x)$ for $T = 35{\cdot}7$ K is plotted in figure 5 for $E = 1000\,\mathrm{V\,cm^{-1}}$ and for $E = 250\,\mathrm{V\,cm^{-1}}$. The minimum is rather far away from the interface. The energy function given by (7) should therefore be valid in the region of the minimum.

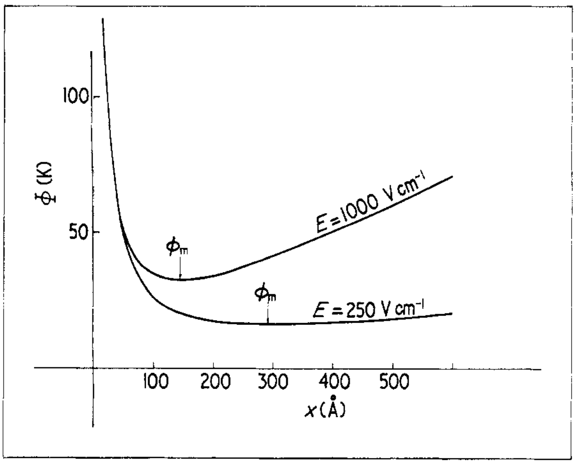

Figure 5. The function $\Phi(x) = A/x + eEx$ plotted for $T = 35{\cdot}7$ K, with $E = 1000\,\mathrm{V\,cm^{-1}}$ and $E = 250\,\mathrm{V\,cm^{-1}}$. The arrows show the x values at which Φ has a minimum in the two cases.

4.3. *The thermal diffusion*

The mean free path of the ions in the liquid neon is much smaller than the width of the potential well. Therefore the mean life τ in the potential well can be analysed with the aid of the Smoluchowski equation (Chandrasekhar 1943)

$$\tau = \frac{2\pi e}{\mu(\Phi''_m \Phi''_0)^{1/2}} \exp(\Delta\Phi/kT) \tag{9}$$

where μ is the ion mobility, $\Delta\Phi$ the barrier height, Φ''_m and Φ''_0 the curvature of the potential energy function at the minimum ($x = x_m$) and at the maximum ($x = x_0$) respectively.

If there are very few ions near the surface, then the electric field E in the liquid is given by (3) and (4), with $\sigma \simeq 0$

$$E_0 = \left(\frac{V_0}{d}\right) \frac{\varepsilon_V}{\varepsilon_L - (\varepsilon_L - \varepsilon_V)\, t/d}. \tag{10}$$

In our case E_0 is not very different from V_0/d. As an example at $T = 30$ K and with $t/d = 0{\cdot}2$, one has $E_0 \simeq 0{\cdot}87\,(V_0/d)$. For higher temperatures and levels the difference $E_0 - (V_0/d)$ is even smaller. The potential energy function is thus given simply by (8), where $E = E_0$. In this case the Smoluchowski equation becomes

$$\tau = \left[\frac{46{\cdot}1A^{1/4}\exp(\Phi_0/T)}{\mu(\Phi_0'')^{1/2}}\right]\left[\frac{\exp(-215A^{1/2}E^{1/2}/T)}{E^{3/4}}\right] \tag{11}$$

where the mean life τ is given in seconds if A is measured in K cm, Φ in K, μ in $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, Φ_0'' in $\mathrm{K\,cm^{-2}}$ and E in $\mathrm{V\,cm^{-1}}$.

When the interactions between the charges in the potential well cannot be neglected, the energy function cannot be written in the simple form (8). Far from the interface it will be $\Phi(x) = (A/x) + eE_L x$, where E_L is the constant electric field in the liquid given by equations (2), (3), and (4). Inside the well it will be

$$\Phi(x) = A/x + \rho(x). \tag{12}$$

The function $\rho(x)$ will not be linear, and the diffusion equation will be different from (11), which is valid only for a homogeneous electric field. This is indeed our case, as we show in figure 6. We have plotted in that figure the values of τ measured at $T = 35{\cdot}7$ K, for three different liquid levels, as a function of the electric field E_0. The experimental points are located on three different curves (one for each level), which are function of E completely different from that given by the formula (11). These facts prove that the electric field E_0 is not a good parameter for the description of the experimental results. The term $\rho(x)$ in potential energy will be the sum of a contribution due to the external field E_0, and of another one given by the charges distributed in the well.

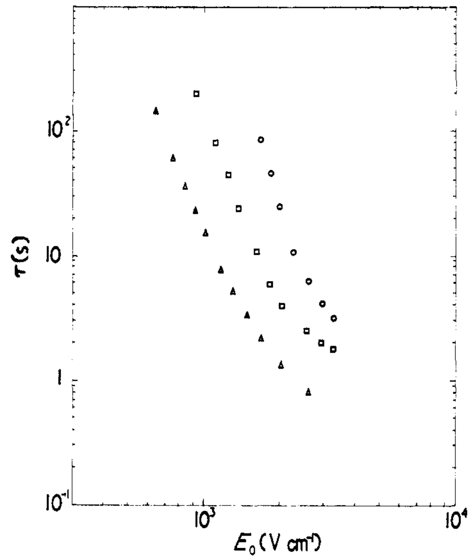

Figure 6. The trapping times τ measured at 35·7 K for different liquid levels, plotted against the electric field E_0 as defined in the text.

The charge distribution changes the potential energy and the mean life τ, and it is in turn a function of the modified potential and of the modified mean life τ. Moreover it depends on the strength of the ionization source. The whole problem is difficult to handle. However our measurements show that the effect of the charge distribution can be accounted for using simply the equation (11), with the electric field E_L in the liquid far away from the interface. We observe at first that the quantity $\ln(\tau E^{3/4})$ must be expected

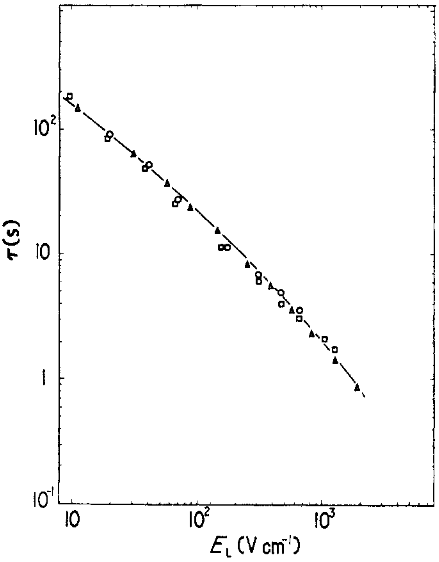

Figure 7. The trapping times τ as those of figure 6 plotted against the electric field E_L. The overall error on τ and E_L can be estimated to be ±10%.

from (11) to be a linear function of $E^{1/2}$, with a slope proportional to $(A^{1/2}T)$. We see in figure 8 that this is the case if one uses the electric field E_L. The straight line in the figure has been drawn with the theoretical slope given by equation (11). The agreement shows that the use of the field E_L is not too incorrect, and that the barrier is really due to the dielectric discontinuity.

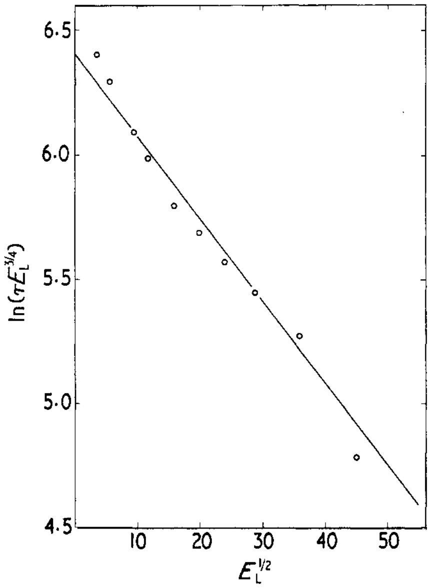

Figure 8. The quantity $\ln(\tau E_L^{3/4})$ plotted against $E_L^{1/2}$ for $T = 35{\cdot}7$ K and $t = 0{\cdot}37$ cm. The straight line has the slope defined by equation (11).

Figure 7 shows the same data as figure 6, but plotted now as a function of the field E_L. We see that the data obtained at three different levels fall along a unique curve, within a good approximation. The dependence of τ on the liquid level can be therefore accounted for with the use of the field E_L. The full curve in the figure 7 is the function

$$\tau = (\alpha/E_L^{3/4}) \exp[-215(AE_L)^{1/2}]$$

where $A = 23{\cdot}4 \times 10^{-6}$ K cm is the appropriate value of A for $T = 35{\cdot}7$ K. The constant α has been chosen to be 910 s (V/cm)$^{3/4}$ in order to fit the experimental points. We see that equation (11) describes the experimental results fairly well over a broad range of the mean life τ. We can conclude that the barrier is due to the dielectric discontinuity, and that the Smoluchowski equation is an appropriate description of the escape mechanism, provided that the field E_L is used. We think, on the other hand, that a theory for the brownian diffusion of interacting particles in a potential well would be very useful at present.

5. Conclusions

The information on the barrier near the interface is contained in the temperature dependent factor

$$\alpha = \frac{46{\cdot}1A^{1/4}}{\mu} \frac{\exp(\Phi_0/T)}{(\Phi_0'')^{1/2}} \tag{13}$$

which enters in equation (11). Its value is deduced from a best fit of the experimental data, as explained above. There are two quantities which are unknown in (13), Φ_0 and Φ_0''. Both of them depend on the details of the barrier near the interface, and are temperature dependent. Therefore in order to get realistic information about the barrier, we need a theory finer than the classic image-force for a sharp dielectric discontinuity. Because such a theory does not at present exist, we can try a first rough discussion assuming $\Phi_0'' =$ constant, and $\Phi_0 = (A/x_c)$, with a constant x_c. In this case we have from (13)

$$H = \ln(\alpha\mu/46{\cdot}1A^{1/4}) = -(1/2)\ln\Phi_0'' + (A/Tx_c)$$

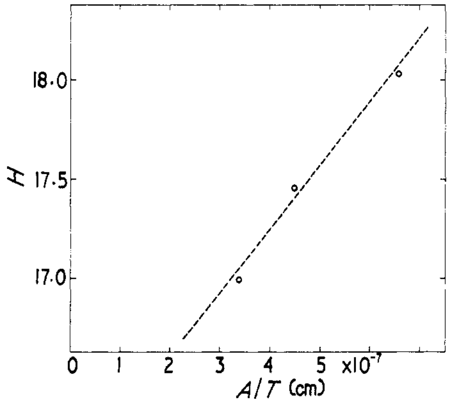

Figure 9. The values of the quantity H measured at three different temperatures plotted as a function of A/T as explained in the text.

so that the quantity H, plotted as a function of (A/T) should give a straight line. The result of the measurements, performed at three different temperatures (35·7 K, 40·7 K, and 42·6 K) are shown in figure 9, from which we get $x_c = 32$ Å and $\Phi_0'' = 3{\cdot}3 \times 10^{-4}$ erg cm^{-2}. The value of the cut-off distance x_c is a reasonable one, not very different from the value $x_c = 25$ Å obtained in helium by Schoepe and Rayfield (1971). The curvature is very low, and very different from the value $\Phi_0'' = 3{\cdot}1 \times 10^3$ erg cm^{-2} obtained in helium by Schoepe and Rayfield.

We think that more experimental work must be done in order to clarify the process occurring when the ion reaches the interface. Experiments at various temperatures and in various fluids, together with an appropriate theory, should also give reliable informations on the liquid–vapour transition region.

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