

Electron mobilities in alkanes through the liquid and critical regions¹

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Three properties of electrons in liquids are governed by scattering at low energies and show similar dependence upon liquid density and molecular shape. They are the mobility, the dependence of the mobility upon electric field strength, and the penetration range of low energy (< 10 eV) electrons. The scattering cross sections of hydrocarbons in the liquid phase (near or below the normal boiling point) are smaller when the molecules are more sphere-like. The degree of sphericity of the molecules in the present series decreases in the order 2,2-dimethylpropane (DMP) > 2,2-dimethylbutane (DMB) > cyclopentane (cP) > *n*-pentane (nP).

Electron mobilities in DMP and DMB measured as functions of the liquid density pass through maxima similar to those observed earlier in argon and xenon. The magnitudes of the maxima decrease in the order Xe > Ar > DMP > DMB. The maxima occur at densities approximately double the critical density d_c . There is a small maximum for electrons in cP, but none for those in nP.

The mobilities in the supercritical gases are similar for the four compounds. The Arrhenius temperature coefficients are all 7–10 kcal/mol (0.3–0.4 eV/electron) for temperatures and densities near the critical values. This implies that electrons form localized states in the gases. The extent of localization in supercritical DMP appears to be greater than that in the normal liquid. The localization is not the critical phenomenon predicted by Lekner.

The mobility in liquid DMP decreases at high electric field strengths. The magnitude of the field dependence changes with the liquid density and passes through a maximum similar to that of the mobility itself. The field dependence in liquid DMB is smaller than that in DMP, but it also passes through a maximum at a density about double d_c .

Equations are given that describe the mobility in nP at all temperatures from the triple point through to the supercritical gas. The electrons reside mainly in localized states over the entire temperature range, but transport occurs mainly in extended states to which the electrons are thermally excited.

The penetration range parameter b_{GP} of secondary electrons in these liquids is normalized for comparison by multiplying by the liquid density d . The values of b_{Gpd} plotted against d form curves similar in shape to the μ against d curves, but the relative variations in b_{Gpd} are much smaller.

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La mobilité des électrons dans un milieu constitue un outil très sensible pour déterminer la diffusion et le transfert d'énergie des électrons thermiques dans ce milieu. Les sections efficaces pour la diffusion et le transfert d'énergie des hydrocarbures en phase liquide (à proximité et en dessous de la température d'ébullition) sont d'autant moindres que la forme des molécules approche la forme sphérique. La sphéricité des molécules dans la présente série décroît dans l'ordre suivant: le diméthyle-2,2 propane (DMP) > le diméthyle-2,2 butane (DMB) > le cyclopentane (cP) > le *n*-pentane (nP). Trois propriétés des électrons dans ces liquides à 295 K décroissent également dans cet ordre. Elles sont: la mobilité des électrons thermiques, la variation de cette mobilité en fonction du champ électrique et les distances de pénétration des électrons de 0.1 à 10 eV.

Les mobilités dans le DMP et DMB, mesurées en fonction de la densité du liquide, passent par un maximum semblable à celui déjà observé dans l'argon et le xenon. Ce maximum apparaît à une densité approximativement double de la densité critique d_c . L'amplitude de ce maximum décroît dans l'ordre suivant Xe > Ar > DMP > DMB. Le maximum est peu visible pour le cP et inexistant pour le nP.

Les mobilités dans les gaz, au delà de la température critique, sont semblables pour les quatre hydrocarbures. Les coefficients de température d'Arrhénius sont tous de 7–10 kcal/mol (0.3–0.4 eV/electron) pour les températures et densités proches des valeurs critiques. Ceci implique que les électrons forment des états localisés dans les gaz et que la localisation au delà du point critique semble être plus importante que dans le liquide en dessous de la température d'ébullition. Cette localisation n'est pas le phénomène critique prédit par Lekner.

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La mobilité dans le DMPr liquide décroît aux champs électriques élevés. L'amplitude de cette dépendance en fonction du champ varie avec la densité du liquide et passe par un maximum similaire à celui de la mobilité. La dépendance en fonction du champ est plus petite pour le DMB liquide que pour le DMPr et le maximum de cette dépendance se situe également à une densité double environ de la densité critique.

Des équations décrivent la mobilité dans le nP à toutes températures depuis le point triple jusqu'au gaz supercritique. Les électrons résident principalement dans des états localisés mais le transport se fait par des états non localisés vers lesquels les électrons sont excités thermiquement.

Afin de comparer les parcours des électrons secondaires b_{GP} dans ces liquides, ils doivent être multipliés par la densité d . Les valeurs de $b_{GP}d$ portées en graphique en fonction de d présentent des courbes semblables aux courbes de μ en fonction de la densité. Toutefois, l'amplitude des variations de $b_{GP}d$ est de beaucoup inférieure à celle de μ .

Introduction

The mechanism of electron transport in materials undergoes a change when the density (1–9) temperature (10–12), or composition (10, 13, 14) of the material is varied over an appropriate range. Although density and temperature were usually varied together, the change of mechanism in a given system has been mainly attributable to one or the other of the properties.

Many different transport mechanisms have been proposed, each fitted to a certain type of system. A general understanding of electron transport has not been attained. For example electron behavior in amorphous solid silicon (15) is similar to that in liquid ethers (16); perhaps the 'ion-like' mechanism of electron transport in low temperature ethers is actually electron hopping between localized states on the edge of the conduction band as proposed for low temperature amorphous silicon. Results are needed from many more systems before a unified theory of electron transport can be formulated.

Experiments involving wide changes of density have involved monatomic fluids (1–9). The present work reports analogous studies with polyatomic molecules. The compounds were chosen to display a wide range of electron mobilities at room temperature.

Experimental

Materials

The hydrocarbons were Phillips Research Grade with initial purities $\geq 99.9\%$. They were further purified as follows: shake or stir 24 h with concentrated sulfuric acid; separate from acid and stir 1 h with solid barium carbonate; pass the vapor through a column of sodium hydroxide pellets; degas; stir 24 h with lithium aluminum hydride; degas; stir 48 h on sodium/potassium alloy; degas; distil into the conductance cell after the latter had been evacuated to 10^{-7} Torr.

Conductance Cells

Two kinds of conductance cells were used, one for low temperatures and pressures (17) and another for pressures up to 100 atm.

A sketch of the high pressure cell is shown in Fig. 1. The distance between the electrodes was determined by a spacer used during manufacture. The cell constant was determined conductimetrically, using standard potassium chloride solutions. The conductance bridge was designed to keep the guard and collector electrodes accurately at the same ac potential (Fig. 2). The cell constant was independent of frequency, 1–3 kHz.

The body of each cell was coated on the outside with Aqua Dag (GC Electronics TV Tube Coat), which was grounded to the copper braid that shielded the lead to the collector electrode. This minimized interference from conductance in the glass. The glass side arm over the high voltage lead was not covered with Aqua Dag or braid because the high fields thus formed in the glass created stresses in it and caused it to break more easily.

A vertical strip of wall on the front and back of the cell was left clean so that the liquid contents could be observed. It was important to note the occurrence of bubbling, the disappearance of the meniscus, and the appearance and disappearance of critical opalescence.

To degas the metal electrodes, the cells during evacuation were heated to a temperature 50 deg higher than that to which they would be raised when containing a sample.

Temperature Control

The low temperature system was the same as that described earlier (17).

For temperatures greater than ambient the cell was positioned on asbestos supports in a clear walled Dewar. A heat gun (Master Appliance Model H67518) was fitted to a 3 cm diameter glass pipe which passed through the asbestos lid, to the bottom of the Dewar. The fan motor and heating coil of the gun were connected to separate Variacs. The heating coil was connected to an LFE Corp. Model 226-A21 temperature controller. Two thermocouples were placed inside the side arm leading to the guard electrode, as near as possible to the body of the cell. One thermocouple was connected to the temperature controller and the other was used to record the temperature. The thermocouples were calibrated by the temperature at which the meniscus disappeared. During heating of the liquid the meniscus stayed in about the center of the cell, well above the electrodes.

The Dewar was placed in a grounded Faraday cage.

Determination of Mobility μ

Electron mobilities at low temperatures in nP were determined from the magnitudes of the electron conductance transients (ect) and the free ion yields (18). Amplifier model 4 (19), with a signal decay half-life of 75 ns and

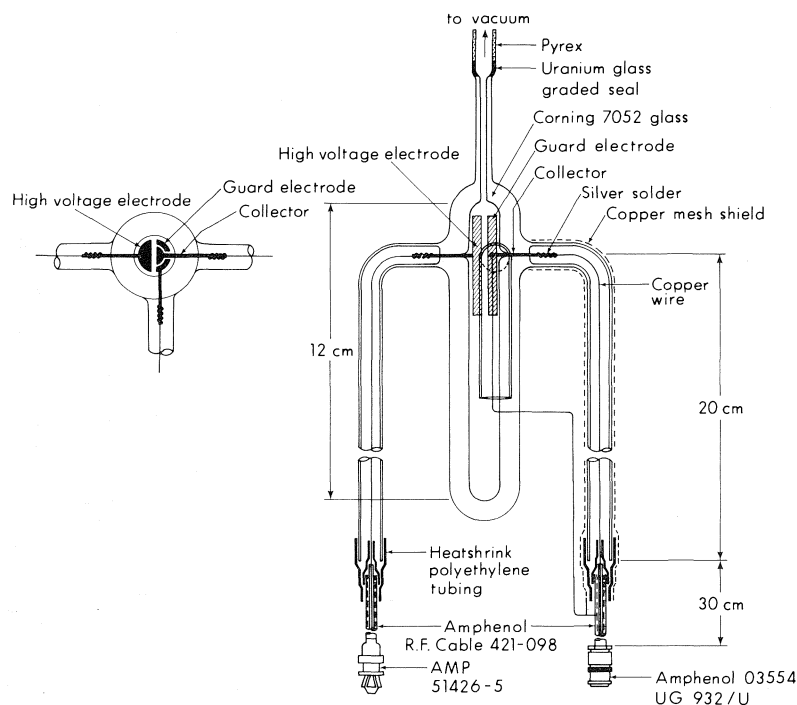


FIG. 1. Conductance cell for studying electrons in critical fluids. The walls were 12 mm thick Corning 7052 borosilicate glass. The electrodes were stainless steel and the pins Kovar. The distance between the electrodes was 3.2 mm and the cell constant 0.125 cm^{-1} .

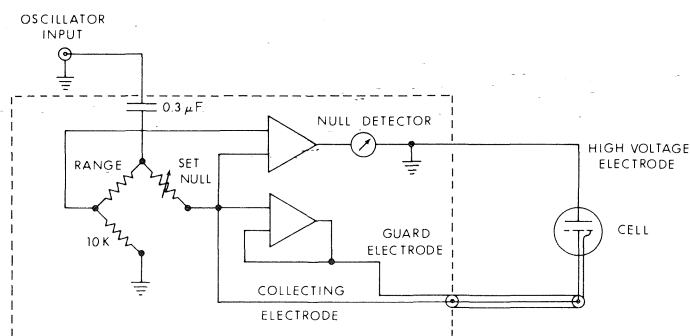


FIG. 2. Bridge circuit used to measure the cell constant. The dashed line represents a metal box which also contained the power supply.

3–97% response time of 200 ns, was used to measure the cell constant.

At high temperatures in nP and under all conditions in the other hydrocarbons, electron mobilities were obtained from the time of flight between the electrodes (eq. 1).

$$[1] \quad \mu = l^2/Vt_d$$

where l is the distance between the electrodes, V is the applied voltage, and t_d is the time required for the charged particle to drift the distance l . An example oscilloscope trace for a time of flight measurement is shown in Fig. 3.

Under conditions where both methods could be used, the mobility values agreed within <10%.

Ion mobilities were determined using [1] and the circuit sketched in Fig. 4.

The radiation pulses were 0.1 or 1.0 μs of 1.7 MeV X rays delivering 0.1 or 1.0×10^{11} eV/g, respectively.

Physical Properties of the Liquids

The densities d for *n*-pentane (nP) and cyclopentane (cP) were obtained from refs. 20–22. Plots of d against T are not available for 2,2-dimethylpropane (DMP) and 2,2-dimethylbutane (DMB), but the densities at 20°C and the critical temperature T_c are known (20, 21). The variation of d with T for DMP and DMB were estimated by using the curves for *n*-butane, *n*-pentane, and *n*-hexane (22) as guidelines.

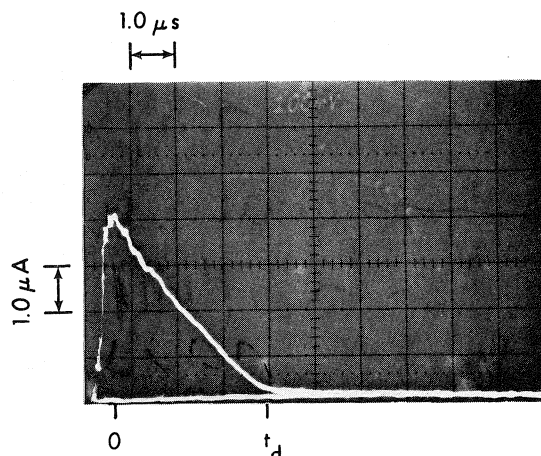


FIG. 3. Oscilloscope trace for an electron time of flight measurement in DMPr at 295 K. Applied voltage = 500 V.

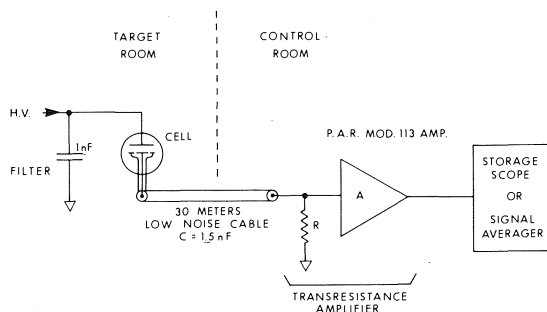


FIG. 4. Apparatus for measuring ion drift times. The 3–97% response time of the input network is $5.2 \times 10^{-9} R$ (s). The transresistance amplifier gain is $R \times A$ (ohm). Typical values of R and A are $10^4 \Omega$ and 10^4 , respectively.

The pressure on the liquid was always its vapor pressure.

The values of the dielectric constant ϵ at various temperatures were calculated using the Lorenz-Lorentz equation (23a) for cP and DMPr, and the Onsager relation (23b) for nP and DMB. A dipole moment $\mu = 0.06$ D (24) was used for the last two compounds, but it made <1% contribution to the dielectric constant even at the lowest temperature. Values of the refractive indices were obtained from refs. 20 and 21.

Results

Temperature Dependence at Low Field Strengths

Electron mobilities ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) in the liquids at 296 K are: nP, 0.12; cP, 1.1; DMB, 11; DMPr, 61. The values for cP, DMB, and DMPr are within 10% of those listed in ref. 25, but there is a scatter of up to $\pm 30\%$ for reported mobilities of electrons in liquid hydrocarbons (11, 18, 25–30). The precision within a given series of experiments is usually <10%. Larger

scatter may occur in results from the same laboratory over a period of years and the reason for it remains unknown. However, electron mobilities may differ by several orders of magnitude from one compound to another, so the 30% uncertainty in the absolute magnitudes does not seriously hinder progress in the investigation of electron behavior in liquids.

The mobility of electrons in nP increases continuously with temperature from 150 K through the critical temperature T_c and in the supercritical gas (Fig. 5). By contrast the mobility in DMPr goes through a maximum in the liquid phase at a temperature 29 deg below T_c , and through a minimum at T_c (Fig. 5).

The behaviors in cP and DMB are intermediate between those in nP and DMPr (Fig. 5). In all cases the curves undergo a change of slope at T_c . The validity of the change of behavior is illustrated in Fig. 6 by the error bars marking the upper and lower limits of the measured values at each temperature.

The mobilities in the four critical fluids all lie

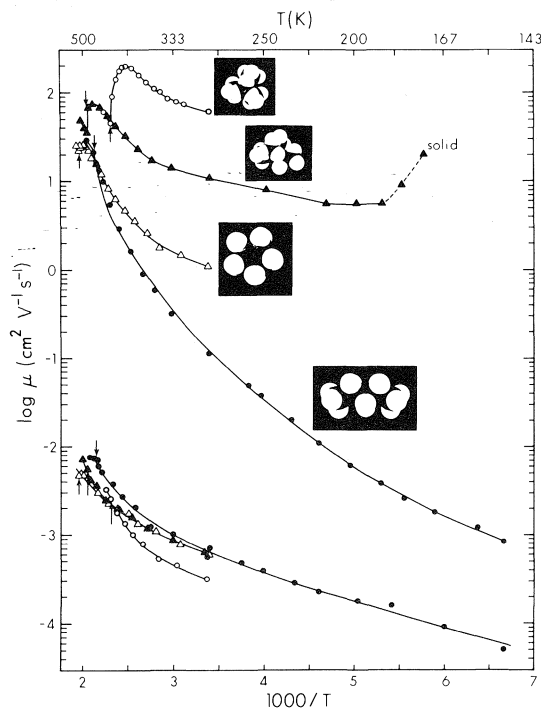


FIG. 5. Effect of temperature on the mobilities of electrons (upper set of curves) and positive ions (lower set) in fluid hydrocarbons. \circ , DMPr; \blacktriangle , DMB; \triangle , cP; \bullet , nP. The arrows mark the critical temperatures of the liquids. The curve through the nP points was calculated from eqs. 2–7.

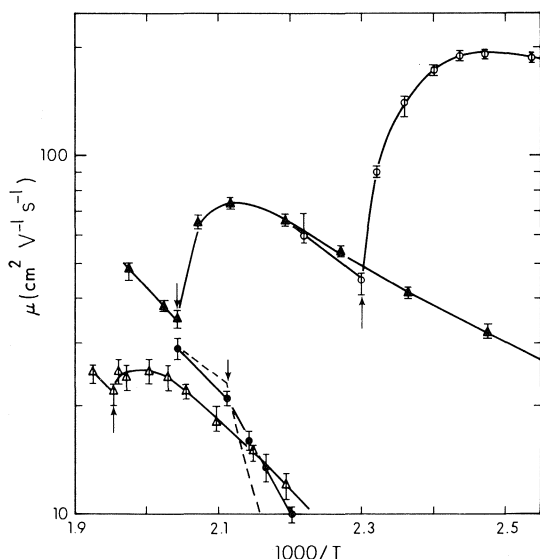


FIG. 6. Behavior of electron mobilities in the vicinity of the critical region in DMPr (\circ), DMB (\blacktriangle), cP (\triangle), and nP (\bullet). The error bars mark the upper and lower limits of the measured values at each temperature. The dashed line represents the calculated curve for nP in this region.

within a factor of two of each other, while at 295 K the differences are up to 500-fold.

The mobilities of heavy positive ions increased monotonously with temperature in all the hydrocarbons (Fig. 5). Extrema are therefore characteristic of electron mobilities. The upward curvature of the ion mobility plots for high temperatures is similar to that in the electron mobility plots at temperatures below the mobility maxima.

Anion mobilities were usually not measured because under most conditions the electrons were swept out of the system before becoming attached to an impurity to form an anion. However, anions were obtained in cP and DMB at the lower temperatures. Compared to the positive ion mobilities in Fig. 5, $\mu_-/\mu_+ = 2.0 \pm 0.1$ in cP and 2.1 ± 0.1 in DMB. Similar values of the ratio have been obtained in many hydrocarbons (31–33).

In the high temperature sample of nP and in DMB, slower positive ions than those recorded in Fig. 5 were also observed. The ratio $\mu_+(\text{fast})/\mu_+(\text{slow})$ had an average value of 2.3 ± 0.2 in nP and 1.9 ± 0.1 in DMB. The slower cations may have been mainly dimers to tetramers of product and impurity olefins.

Electric Field Dependence

In nP and cP the electron mobilities were in-

dependent of applied field strength over the range 3–20 kV/cm in liquids and 3–12 kV/cm in the supercritical gases. Experimental difficulties prevented measurements at higher fields at the highest temperatures. The difficulties included amplifier sensitivity and response time and field induced conductance switching in the hot glass (34).²

The electron mobility in DMPr at 295 K decreased gently with increasing field strength at $E > 4$ kV/cm. Upon raising the liquid temperature, the mobility and its field dependence increased (Fig. 7). Both the mobility and its field dependence passed through maxima at temperatures near 400 K (Figs. 7 and 8). For a given mobility, the field dependence was smaller on the high than on the low temperature side of the mobility maximum. A few degrees below T_c the field dependence became negligible up to 20 kV/cm and remained so in the supercritical gas (Fig. 8). The mobility passed through a minimum in this temperature region (Fig. 6).

The behavior was similar in DMB (Figs. 9 and 10), but the mobilities and their temperature dependences were smaller than in DMPr.

Cation mobilities were independent of applied field strength in the present region.

Discussion

Electrons in liquid alkanes are distributed among localized and extended states. The measured mobility is an appropriate average of the mobilities characteristic of the states, taken over the distribution of the electrons among the states. These things depend on the temperature and density of the liquid and on the nature of the molecules. The influences of all three factors are visible in Fig. 5.

Effect of the Nature of the Molecules at

$$T \ll T_c$$

The molecules of the present liquids are non-polar or only slightly polar, with gas phase dipole moments ≤ 0.1 D (24). The potential wells of the localized states of electrons in the liquids are at most a few tenths of an eV deep. The traps tend to be shallower when the molecules are more sphere-like (27). Electrons also appear to be less efficiently localized in traps the

²Field induced switching occurs in many amorphous materials such as boron-based glasses (34). Recently, most studies of the phenomenon have been made with chalcogenides (34–36).

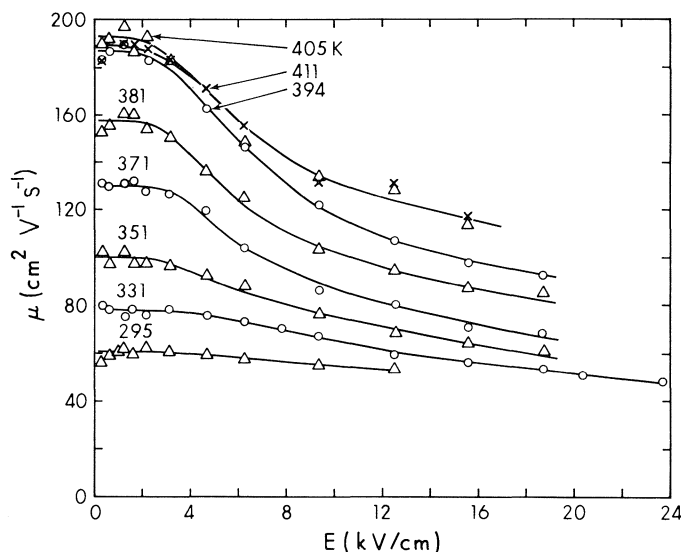


FIG. 7. Electric field dependence of electron mobilities in liquid DMPr at temperatures from 295 K through those at the mobility maximum.

more easily the molecules can rotate in the fluid (18).

The mobilities of electrons in extended states are several orders of magnitude greater than those in localized states. Thus the measured mobilities are greater in liquids of the more sphere-like molecules: nP < cP < DMB < DMPr (Fig. 5).

Effect of Temperature

In nP at the lowest temperature the electron mobility is eightfold greater than that of the anions, and the ratio increases with temperature. The contribution of an ion-like mechanism (12) to electron transport in liquid alkanes therefore appears to be negligible.³ The mobility and its temperature dependence can be explained in terms of thermal partition of the electrons between localized and extended states, with transport occurring mainly in the latter (38).

The energy states are affected by local fluctuations in the molecular orientation and density

³The ion-like mechanism in liquid ethers is conceptually similar to thermally assisted tunnelling to nearest neighbor centers (35) and small polaron hopping (37). It does not involve migration of the solvation shell of the electron (12). The similarity between the activation energies of electron and ion mobilities in polar liquids had been rationalized in terms of the energy requirements of rotational-translational motions of the anisotropic solvent molecules (16). However, the striking resemblance between the behavior of electrons in a specimen of solid, amorphous silicon (37), and that in liquid ethers (16) is difficult to understand.

of the fluid (39). It is assumed that the distribution of transition energies from localized to extended states is a Gaussian centered about a value E_0 , with a distribution parameter σ .

$$[2] \quad N(E) = \pi^{-1/2} \sigma^{-1} \exp[-(E - E_0)^2 / \sigma^2]$$

where $\pi^{-1/2} \sigma^{-1}$ is a normalization factor. The measured mobility μ_e is given by [3], where μ^0 is

$$[3] \quad \mu_e = \mu^0 \int_{-\infty}^{\infty} N(E) [1 + \exp(E/kT)]^{-1} dE$$

the mobility in the extended state. It is assumed that the entropy change is small for an electron going from a localized to an extended state and that the energy ranges of the localized and extended states overlap (12).

To calculate μ_e from [3] one requires values of μ^0 , E_0 , and σ . Unique values of the parameters in a given system are not available, but reasonable limitations can be put on them by comparison with other data. By analogy with the temperature dependences of the optical absorption parameters of solvated electrons (12), one may assume that $dE_0/dT \leq 0$ and $d\sigma/dT \geq 0$. Due to the Franck-Condon requirement of optical transitions and the probability that there are only one or two bound levels per electron trap in a liquid alkane, one may take $E_0 \leq E_{am}$, where E_{am} is the transition energy at the optical absorption maximum. The values of E_{am} in nP over the temperature range 150-

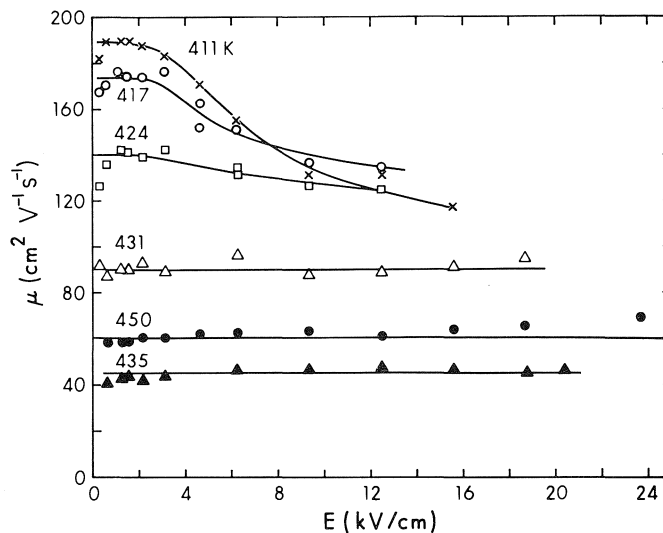


FIG. 8. Electric field dependence of electron mobilities in DMPr at temperatures above that of the mobility maximum. $T_c = 434$ K. The filled points refer to the gas at a density of 0.242 g/cm³.

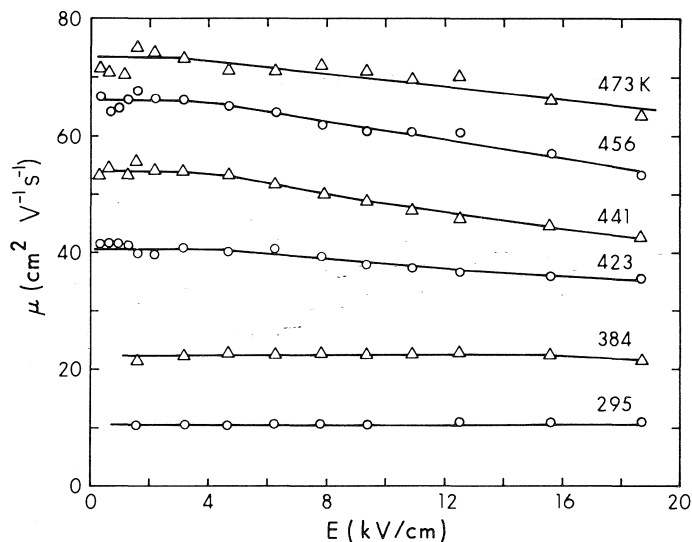


FIG. 9. Electric field dependence of electron mobilities in liquid DMB at temperatures from 295 K to that of the mobility maximum.

500 K are probably near 0.6–0.3 eV (12, 40). The value of $d\sigma/dT$ for the electron transitions is probably not greater than that of the thermal energy fluctuations in the liquid, so $d\sigma/dT \leq (2kC_p)^{1/2} \approx 5 \times 10^{-4}$ eV/K in nP at $T < 400$ K (22, 38).

In earlier studies over more limited temperature ranges μ^0 has usually been taken to be independent of temperature (12, 25, 28, 30). That approximation is inadequate for the wide ranges

of temperature and fluid density in the present work. In particular, the rapid change of density at temperatures approaching T_c should be taken into account, although the way to do it is not straightforward. For electrons in nP it was assumed that the mean free path λ was inversely proportional to the density, and that μ^0 could be represented by [4] (12), where v^0 is the jump

$$[4] \quad \mu^0 = \lambda^2 v^0 e / 2kT$$

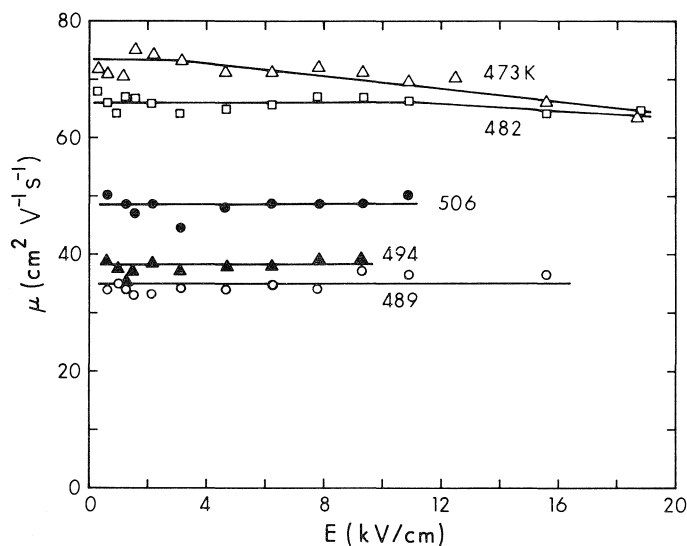


FIG. 10. Electric field dependence of electron mobilities in DMB at temperatures from the mobility maximum to the supercritical region. $T_c = 489$ K. The filled points refer to the gas at a density of 0.240 g/cm³.

attempt frequency and e is the unit electronic charge.

Within the above limitations we were able to fit the electron mobilities in nP over most of the liquid range and in the supercritical gas (Fig. 5) with the following parameter values.

$$[5] \quad E_0 \text{ (eV)} = 0.64 - 7 \times 10^{-4} T$$

$$[6] \quad \sigma \text{ (eV)} = 0.15 + 8 \times 10^{-5} T$$

$$[7] \quad \mu^0 \text{ (cm}^2 \text{ V}^{-1} \text{ s}^{-1}) = \mu_{\text{ref}}^0 \left(\frac{d_{\text{ref}}}{d_T} \right)^2 \left(\frac{T_{\text{ref}}}{T} \right) \\ = 250 \left(\frac{0.623}{d_T} \right)^2 \left(\frac{295}{T} \right)$$

where μ_{ref}^0 and the density d_{ref} are the values at the reference temperature T_{ref} . The fit is adequate over the entire 350 deg range of temperature except for a 30 deg region just below the critical temperature (Figs. 5 and 6). In this region the density changes rapidly and nonlinearly with temperature, so [5] and [6] become inadequate representations of E_0 and σ , respectively.

The transition energy E_0 is equal to $(V_0 - \bar{V})$, where V_0 is the energy of an electron in the lowest extended state relative to the vacuum level, and \bar{V} is the mean energy of electrons in localized levels (38, 39, 41–43). Preliminary treatments of electron mobilities by fluctuation theories (39, 41) neglected the temperature dependence of E_0 and, based upon thermal energy

fluctuations, assumed $d\sigma/dT = 6\text{--}11 \times 10^{-4}$ eV/K for C_5 and C_6 hydrocarbons. However, to fit the temperature dependence of the mobilities using such large values of $d\sigma/dT$ would require that dE_0/dT be positive and of similar magnitude (38). Positive values of dE_0/dT are unlikely, so the temperature coefficient of σ must be much smaller than that of the dispersion parameter of thermal energy fluctuations.

Holroyd and co-workers (42, 43) have measured the photoinjection of electrons from metal surfaces into liquids and into a vacuum as functions of photon energy and applied electric field strength. From the difference between the injection energy into a liquid and into a vacuum they derived an energy that was equated to V_0 . They obtained $dV_0/dT = -2.2 \times 10^{-3}$ eV/K for nP (43), which is much greater in magnitude than the temperature coefficient of E_0 in [5]. This implies that the energies of the localized and extended states in alkanes are affected similarly when the liquid temperature is changed. Thus V_0 and \bar{V} in alkanes appear to be affected mainly by the changing density; $(dV_0/dd) \approx (d\bar{V}/dd) =$ positive, which multiplied by the negative (dd/dT) gives the observed results. There would be a positive contribution from $(d\bar{V}/dT)$ due to decreased orientational polarization at higher temperatures, but it would be relatively small in hydrocarbons.

The direct effect of density on electron energy

levels in liquids, distinct from its secondary effect through the dielectric constant, has also been detected through the influence of pressure on optical absorption energies in alcohols (44–46), and through the influence of temperature on V_0 in hydrocarbons (43).

Electron migration in nP remains in the thermally activated regime even in the supercritical gas. The mobility increases monotonously with temperature. By contrast, the mobility in DMPr goes through a maximum (Fig. 5). The maximum occurs at a temperature 29 deg below T_c , so the decrease in mobility at high temperatures is not a critical phenomenon. The behavior is reminiscent of that in argon (2) and xenon (5), where the electrons were presumed to normally reside in the lowest extended state (47). Changes in mobility would then reflect changes in μ^0 . However, μ_e increases with temperature in the supercritical gas of DMPr at constant density, just as it does in nP (Fig. 6). It appears that electron transport in supercritical DMPr occurs by a two state mechanism and that the decrease of μ_e at $T > 405$ K is due to the formation of localized states. The Arrhenius activation energies of μ_e in all four of the present supercritical gases are 7–10 kcal/mol (0.3–0.4 eV/electron). They are about double that in liquid nP at room temperature, where the two state mechanism is generally accepted.

The mobilities and their temperature dependences in DMB and cP are intermediate between those in nP and DMPr (Fig. 5). Assuming that the values of σ are similar in the four hydrocarbons, the variations of μ_e with temperature indicate that the relative values of E_0 at a given temperature at $T \ll T_c$ decrease in the order nP > cP > DMB > DMPr. Measured values of V_0 at ~ 296 K lie in the same order (42, 48).

An adequate interpretation of mobility maxima in fluids has not yet been found (2, 49), so theoretical curves are not offered for the DMPr, DMB, and cP results in Fig. 5.

Effect of Density

The mobilities are displayed as functions of the liquid densities in Fig. 11. Points for solid DMPr (29) and DMB are included.

The increase in mobility on going from the liquid to the crystalline solid is due to the smaller amount of scattering in the more ordered medium (represented by a smaller structure factor (50)). The continued increase of μ_e with increasing density of the solid is actually due to the

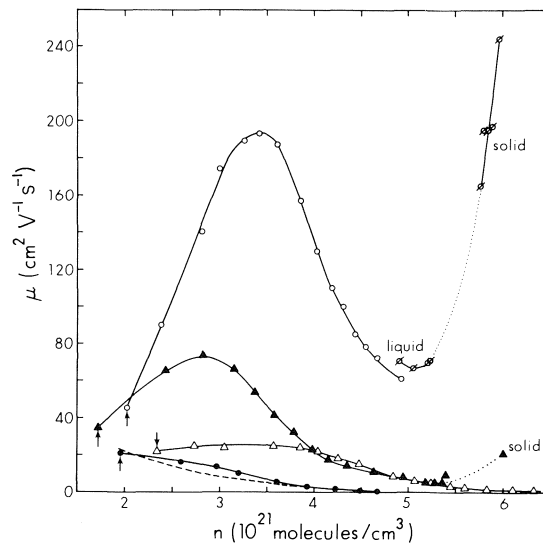


FIG. 11. Electron mobilities in DMPr (○), DMB (▲), cP (△), and nP (●) plotted against the molecular density of the medium. The arrows mark the critical fluids. The liquid and solid phase results for DMPr from ref. 29 are also included (◊). Dotted lines mark the liquid–solid transition. The dashed line for nP represents the mobilities calculated from eqs. 2–7. The densities were changed by changing the temperature of the samples under their vapor pressure.

decreasing temperature of the samples (29), and thereby reduced scattering of the electrons by phonons (51).

Upon decreasing the density of liquid DMPr from that at the triple point, the mobility passes through a minimum. The increase of μ_e with decreasing density is attributed to a decreasing scattering length. The molecules in the normal liquid are so close together that an electron passing between them suffers mainly repulsion from the hard cores (Hartree fields) of the molecules (51). As the density decreases the molecules move farther apart and the electron experiences more of the attractive polarization interactions, which tend to counteract the hard core repulsions. The scattering length thereby decreases. The attractive interaction continues to increase with decreasing fluid density and at some point cancels the hard core repulsion, and the scattering cross section is a minimum. Upon further reducing the density the attractive polarization dominates the electron–molecule interaction, the scattering length becomes negative, and the scattering cross section increases again. The mobility therefore decreases. This model has been used to interpret the mobility maximum in

liquid argon (47). However, there are quantitative difficulties with the model (2, 49). Some other process contributes to limiting the mobility at the maximum and on the low density side of the peak. The present results from fluid hydrocarbons indicate that the other process is electron localization. Lekner and Bishop (4) proposed that localization would take place in simple fluids near the critical point. An effect that is peculiar to the critical region does not occur (5), but localization does take place over a broader range of densities.

The data in Table 1 and in Fig. 11 of ref. 2 indicate that electron migration in fluid argon gradually changes to a thermally activated two state mechanism at densities below 1.4×10^{22} atom/cm³. The mobility maximum occurs at 1.2×10^{22} atom/cm³. At 1.0 and 0.7×10^{22} atom/cm³ the Arrhenius temperature coefficients of the mobilities are each 3 kcal/mol. Thus the formation of localized states could make a major contribution to limiting the mobility in this density region.

The maxima in DMB and DMPr occur at 2.8 and 3.4×10^{21} molecules/cm³, which are 1.7 times the respective critical densities. The mobility maxima in argon and xenon occur at 12×10^{21} molecules/cm³ (2, 5), which are respectively 1.5 and 2.4 times d_c .

The mobility in nP appears to be approaching a maximum at the critical point (Fig. 11). The complex behavior in all the hydrocarbons at densities $< 4 \times 10^{21}$ molecules/cm³ indicates why the simple calculations based on [2]–[7] gave poor agreement between calculated and observed mobilities for nP in this region (Fig. 11).

The electron mobility curve for each hydrocarbon in Fig. 5 changes slope abruptly at the critical temperature. The change of slope does not signify a change in electron behavior, but rather a discontinuity in dd/dT . As T_c is approached in the liquid phase the density decreases rapidly and the density effect dominates the change in μ_e . At $T > T_c$ the density remains

constant, so the mobility is affected only by the change of T .

Ion Mobilities

The temperature dependences of ion mobilities in the liquid alkanes within 100 deg of their critical temperatures are non-Arrhenius (Fig. 5). The same is true of the temperature dependences of the viscosities (22) and self-diffusion coefficients (52). The non-Arrhenius behavior reflects the accelerating value of dV_f/dT in this temperature range, where V_f is the free volume.

The relationship between the positive ion mobility μ_+ (cm² V⁻¹ s⁻¹) and the viscosity η (cP) for nP between 230 and 450 K is approximately given by [8], while that for cP between 300 and 420 K is [9]. The calculated and experi-

$$[8] \quad \mu_+ = 1.0 \times 10^{-4} \eta^{-1.3}$$

$$[9] \quad \mu_+ = 2.2 \times 10^{-4} \eta^{-1.1}$$

mental results are displayed in Fig. 12. The mobility-viscosity relationship varies with the structure of the solvent molecules, but is similar for alkanes and ethers (16). Ions in cyclo-solvents have higher mobilities than those in *n*-alkyl solvents of the same viscosity. The mobilities do not fit Walden's rule; the viscosity exponents are -1.1 to -1.3 instead of the predicted -1.0 .

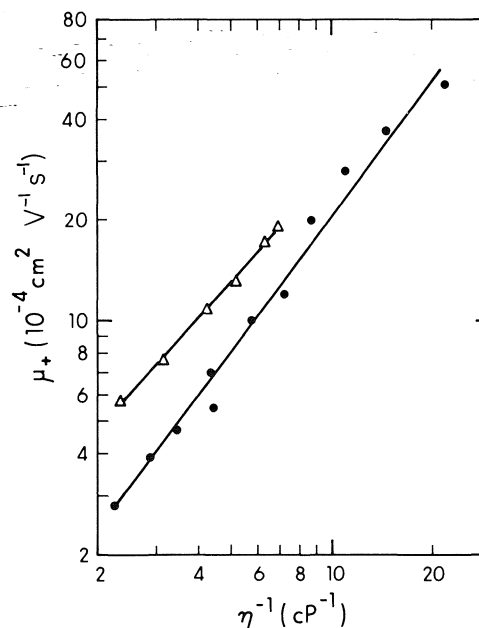


FIG. 12. Ion mobilities in cP (Δ) and nP (\bullet) as functions of the inverse viscosity. The full lines represent [8] for nP and [9] for cP.

TABLE 1. Critical properties of the hydrocarbons

	T_c (K)	P_c (atm)	d_c (g/cm ³)	ϵ_c
Cyclopentane	512	44.6	0.270	1.29
2,2-Dimethylpropane	434	31.6	0.23	1.27
<i>n</i> -Pentane	470	33.3	0.232	1.27
2,2-Dimethylbutane	489	30.9	0.240	1.27

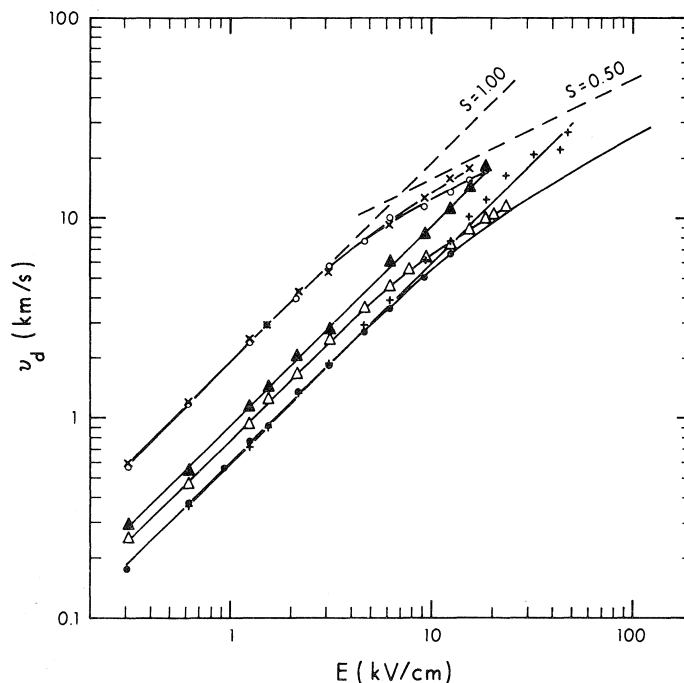


FIG. 13. Electron drift velocity v_d as a function of electric field strength in DMPr at different temperatures. ●, 295 K; △, 331 K; ○, 394 K; ×, 405 K; ▲, 431 K; +, 450 K (gas). $T_c = 434$ K. The curve beyond 13 kV/cm at 295 K represents results from ref. 56.

Rotational motions of the irregularly shaped solvent molecules are required to facilitate ion migration, to maintain the polarization energy at a reasonably low level while the ion moves. The temperature coefficient of rotational motion E_r is often greater than that of shear viscosity E_η ; for water and for diethyl ether $E_r/E_\eta = 1.2$ at 293 K (calculated from data in refs. 53 and 54). Equations 8 and 9 imply that $E_{\mu_+}/E_{\eta-1} = 1.2 \pm 0.1$ in cP and nP, which indicates a correlation between μ_+ and τ^{-1} .

Walden's rule is an approximation, the validity of which stems from the interdependence of rotational and translational motions in these liquids. The rule would be expected to apply more accurately to liquids made up of spherical molecules.

Field Dependence

The electron mobilities in nP and cP are relatively low and they are independent of applied electric field strength up to 20 kV/cm. In DMB and DMPr the mobilities are relatively high and field dependent. The two properties tend to increase together (Figs. 7–10).

The usual way to display field dependence is

to make a log-log plot of drift velocity v_d against field strength (Fig. 13). Field dependence occurs where the slope deviates from unity. It means that the energy acquired by the electron from the field is not dissipated efficiently enough, and the average electron energy increases above thermal. The lower the field at which deviation occurs, the less efficient are the energy loss processes.⁴

If deviation occurs when v_d is only about twice the speed of sound in the medium, the electron energy is dissipated mainly to acoustic phonons. At higher drift velocities more efficient processes are important (50, 55).

In DMPr at 295 K the mobility becomes field dependent when v_d exceeds about 3 km/s (Fig. 13). The present result agrees with that of Bakale and Schmidt (56). By extrapolation of data for other alkanes at the same temperature and at the same density (57), the velocity of sound in liquid DMPr at 295 K is 1.0 km/s. As the temperature of the liquid increases the velocity of sound de-

⁴This explains why the penetration ranges of epithermal electrons are greater in systems that show a greater field dependence of the mobility. Density normalized ranges tend to be greater when the energy loss processes are less efficient.

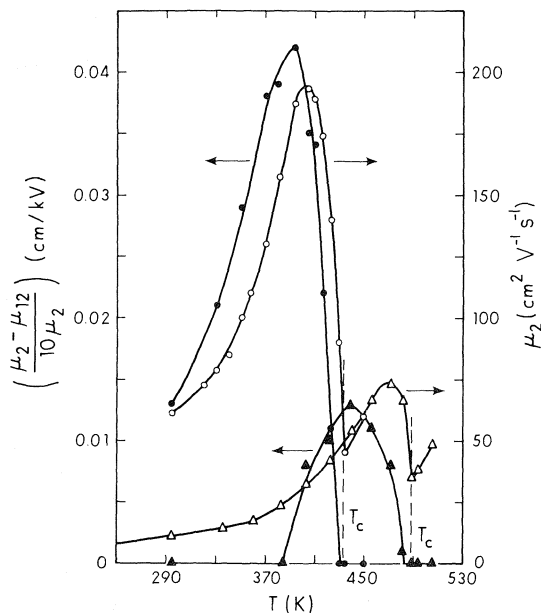


FIG. 14. Electric field dependence of the electron mobilities in DMPPr (●) and DMB (▲) as functions of temperature. μ_2 and μ_{12} are the mobilities at 2 and 12 kV/cm, respectively. Values of μ_2 are also plotted so that the peaks can be compared.

creases (57), whereas the threshold drift velocity for field dependence goes in the opposite direction (Fig. 13). Electron thermalization in DMPPr and the other hydrocarbons cannot be attributed to interactions with the collective motions of acoustic phonons. It must be due to more efficient interactions with motions of smaller groups of molecules.⁵

Simple theories (50) predict that at high fields the drift velocity will vary as $E^{1/2}$. For this reason it is usual to place reference lines with slopes $s = 1.00$ and 0.50 in graphs like Fig. 13. However, a survey of the literature provides little support for the existence of extended regions where $v_d \propto E^{1/2}$ in liquids. The slope simply becomes different from unity and can become as low as zero.

The field dependence varies with the temperature in a manner similar to the mobility itself. A comparative measure of the field dependence is $\mu^{-1} (d\mu/dE)$. In the present work it may conveniently be represented by $(\mu_2 - \mu_{12})/10\mu_2$, where the subscripts denote the field in kV/cm

⁵Terms for these motions in liquids are not well defined. They include optical phonons, rotational-translational oscillations, librations, lattice vibrations, and perhaps others.

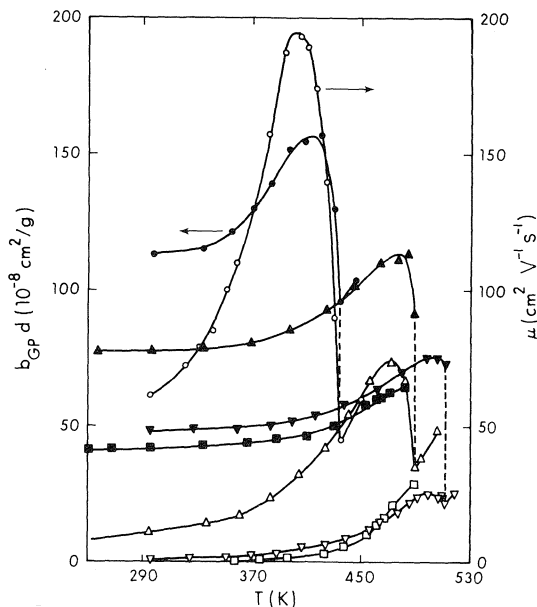


FIG. 15. Density normalized ranges (b_{Gpd}) of secondary electrons in fluid hydrocarbons as functions of temperature. ●, DMPPr; ▲, DMB; ▼, cP; ■, nP; data from ref. 58. The mobilities (open points) are plotted for comparison. The vertical dashed lines mark the critical temperature of each fluid.

at which the mobility was measured and the units of the ratio are cm/kV. Values of this ratio peak about 10 deg below the temperature of the mobility maxima in DMPPr and about 30 deg below the mobility maximum in DMB (Fig. 14). There is a remarkable coincidence between the relative sizes of the mobility and the field dependence peaks.

The density normalized penetration ranges of the secondary electrons in these liquids also pass through maxima (58). The range maxima occur at temperatures slightly higher than those of the mobility maxima (Fig. 15). The relative magnitudes of the range peaks are much smaller than those of the mobility and field dependence peaks. The major portion of the range is generated by electrons in a higher average energy state, probably a few tenths of an eV, while the mobility and its field dependence are properties of electrons having an average energy of a few hundredths of an eV.

The common factor that influences these three quantities is the electron energy transfer cross section. The cross section in liquids comprised of globular molecules first decreases, then increases as the density of the fluid decreases. The molecules of nP are distinctly nonsphere-like; the

scattering cross section in that liquid is relatively large and decreases monotonously with decreasing density at high temperatures.

Electron localization occurs when the scattering cross section is large. Localization apparently occurs in the supercritical gases near the critical region.

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Discussion

J. K. Baird: I wish to point out that I have integrated the Schrodinger equation numerically for argon with the following potential $V(r)$:

$$V(r) = V_{\text{HF}}(r) - \frac{1}{2} \frac{\alpha e^2 f}{(r^2 + r_c^2)^2}$$

where $V_{\text{HF}}(r)$ is the Hartree field, α is the polarizability, e the electron charge, f the screening function, and r_c is a cut-off radius. The screening function may be either that due to Lekner (Phys. Rev. **158**, 130 (1967)) or one based on the Onsager reaction field (J. K. Baird, J. Phys. Chem. **79**, 2862 (1975)). The difference is unimportant except to say that $f = 1$ at zero density and decreases toward zero as the density increases. The cut-off radius r_c was determined so that when $f = 1$, the potential predicted an energy dependence of the total scattering cross section in agreement with that observed in numerous experiments on the Ramsauer effect in low pressure gases. The result of using the above potential to calculate the scattering cross section as f decreased from unity was: (1) the Ramsauer minimum in the cross section persisted; (2) the energy at which the minimum occurred decreased; (3) the value of the cross section at the minimum decreased. It is my view that the above potential is the one from which the single atom cross section in the liquid should be calculated. To take into account diffraction effects, I believe that this cross section should be multiplied by the liquid structure factor, as in the Ziman weak scattering theory, to obtain the many atom scattering cross section in the liquid. Hence, since the single atom cross section appears to decrease with increasing density, one is tempted to conclude that the decrease in the screening function may account for the large electron mobility observed in liquid argon.

Y. Hatano: Do you have any experimental data on the hydrogen isotope effect of μ_e , such as μ_e 's for CH_4 , CH_3D , CH_2D_2 , CHD_3 , and CD_4 , or μ_e 's for C_2H_4 , $\text{C}_2\text{H}_3\text{D}$, $\text{C}_2\text{H}_2\text{D}_2$ (*trans*- $\text{C}_2\text{H}_2\text{D}_2$, *cis*- $\text{C}_2\text{H}_2\text{D}_2$, asym- $\text{C}_2\text{H}_2\text{D}_2$), C_2HD_3 , and C_2D_4 ? One may expect to get an interesting feature for the effect of molecular structure of μ_e .

G. R. Freeman: I agree that the isotope effect should exist. We tried to do measurements in the series of deuterated methanes several years ago, but failed due to impurity problems. We are going to try again soon. As a final comment, on several occasions during the conference experimentalists have presented evidence that behavior similar to the (gas phase) Ramsauer-Townsend effect can occur in simple liquids. The opinion of concerned theoreticians seems to be that the Ramsauer-Townsend effect cannot occur in liquids. At this point we must specify conditions more precisely. In mobility experiments the effect appears as a maximum in a plot of electron mobility against applied electric field strength. The mobility maximum occurs in both gaseous and liquid xenon. For the liquid phase, beginning at the critical density and proceeding towards higher densities, the low field mobility increases and the Ramsauer-Townsend maximum becomes less prominent (Kimura and Freeman. To be published). Thus, the Ramsauer-Townsend mobility maximum (scattering minimum) correlates with the density dependence of the mobility at low fields. What we lack is a formal theory that relates the two effects to common underlying properties of the fluid. Lekner's model for the density dependence of the scattering length (Phys. Lett. A, **27**, 341 (1968)) seems an appropriate place to start.