

Excess Electrons and Positive Charge Carriers in Liquid Methane. I

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(Z. Naturforsch. **28 a**, 511–518 [1973]; received 27 December 1972)

The drift velocities of radiation-induced excess electrons and positive charge carriers in liquid methane were measured at different electric field strengths and several temperatures. For the excess electrons the drift velocity increases up to 1.5 kV cm^{-1} proportional to the electric field strength and a mobility of $(400 \pm 50) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T = 111^\circ \text{K}$ was obtained. Above 1.5 kV cm^{-1} the drift velocity varies with $E^{1/2}$. The temperature coefficient of the mobility is negative. For the positive charge carriers the measurements were carried out up to electric field strengths of 50 kV cm^{-1} and the drift velocity remained proportional to the field giving a mobility of $(2.5 \pm 0.5) \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $T = 111^\circ \text{K}$. The mobility increased with increasing temperature.

The reaction of excess electrons with oxygen was also studied and a rate constant of $8.4 \cdot 10^{11} \text{ l mole}^{-1} \text{ s}^{-1}$ was obtained.

1. Introduction

The physical properties and the chemical behavior of excess electrons in dielectric liquids have received increasing interest during recent years. On one hand the transport properties of excess electrons in simple liquids, e.g. liquefied rare gases, were studied with the objective of describing conducting states in disordered systems¹. On the other hand electron scavenging experiments in hydrocarbons were carried out in order to investigate the inhomogeneous distribution and the reactions of radiation induced charge carriers in these liquids^{2, 3}.

During the last decade a considerable amount of information on the physical properties of excess electrons in rare gas liquids has accumulated. The main contribution came from measurements of the electrical mobility. Excess electrons with mobilities of 10^{-2} to $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were found to exist in liquid helium^{4, 5} and liquid neon⁶. Theoretical investigations have lead to the picture of the electron being localized in a bubble in these liquids.

Mobility values of the order of 10^2 to $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were found for excess electrons in liquid argon, krypton and xenon^{7–9}. A quasifree state has been assumed and theoretical models were developed which explain some of the experimental data^{1, 10}.

More recently, excess electrons have also been observed in carefully purified hydrocarbons^{11–21}. The mobility values measured for various alkanes show a marked correlation with the structure of the molecules. For instance in n-hexane an excess electron

mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained while in neopentane a value of about $70 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was measured. The mobility was independent of the electric field up to the highest field strength applied, i.e. 100 kV/cm in n-hexane and 15 kV/cm in neopentane¹⁵. The temperature dependence of the electron mobility followed the Arrhenius equation with the lower mobility values having the greater activation energy. Neopentane exhibited 0.5 kcal/mole ^{17, 19} while for n-hexane 4 to 5 kcal/mole were found^{15, 16}. The activation energy for the electron mobility in mixtures of neopentane and n-hexane varied almost linearly with the mole fraction of the n-hexane¹⁷. Summarizing these details, DAVIS, SCHMIDT and MINDAY concluded that a trapping model could explain the observed data^{17, 21}. Furthermore, from a modification of the Cohen-Lekner theory for quasifree electrons in polyatomic systems²² they concluded that the electron mobility should remain virtually field strength independent in liquid hydrocarbons²³. For neopentane they predicted the electron mobility to become field strength dependent for values of $E > 400 \text{ kV cm}^{-1}$.

Since FUOCHI and FREEMAN¹⁸ had inferred a mobility of $300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for excess electrons in liquid methane at $T = 120^\circ \text{K}$ from conductivity measurements of irradiated methane, it seemed to be of special interest to study the dependence of the electron drift velocity on the electric field strength. In addition, measurements of the mobility at different temperatures could provide valuable information for the evaluation of the current theory.

Positive excess charge carriers have been investigated in some liquefied gases and in liquid

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hydrocarbons^{24, 25}. The observed mobilities are much lower than the values obtained for excess electrons and range from 10^{-2} to 10^{-4} cm² V⁻¹ s⁻¹. Some models have been developed which make use of Stokes equation^{26, 27}. For the positive excess charge carriers in liquefied rare gases a statistical theory of transport phenomena in monoatomic dense fluids was applied to the interpretation of mobilities²⁸.

The existence of positive charge carriers with higher mobility in cyclohexane was implied in the time-dependent electron and positive ion scavenging study of RZAD et al.². MOZUMDER²⁹ in his diffusion model for neutralization and charge scavenging in dielectric liquids had to assume a faster positive species than hitherto observed in order to obtain agreement with experimental data.

Recently HUMMEL et al.³⁰ have observed the reaction of radiation-induced fast positive parent species with solutes in cyclohexane and n-hexane by pulse radiolysis.

No data on the electrical properties of excess positive charge carriers in liquid methane have been published thus far. We, therefore, measured the mobility and studied the temperature dependence in order to obtain information on the charge transport mechanism.

A short communication on our mobility measurements has been published³¹.

2. Experimental

2.1 Principles of Measurements

The principle of the method employed for the measurement of the mobility consisted in generating instantaneously a uniform concentration of charge carriers of either sign between the plates of a parallel plate ionization chamber. Under the influence of the applied electric field the charge carriers move toward their respective electrodes. This ionization current decays in time until all charge carriers have been swept out of the volume between the plates. Generally, the decay curve will be composed of two parts distinctively separated in time if the mobilities of the positive and negative carriers are very much different. Provided that the initial concentration is sufficiently small, then the decay curve consists of two straight lines each of which is given by

$$i_n(t) = i_n(0) (1 - t/t_n) \quad (1)$$

and

$$i_p(t) = i_p(0) (1 - t/t_p) \quad (2)$$

with t_n and t_p being the drift times for the negative and positive charge carriers to cross the liquid gap d between the plates.

The drift velocity is given by

$$v_{n,p} = d/t_{n,p} \quad (3)$$

and if the drift velocity is proportional to the electric field E the mobility $\mu_{n,p}$ is obtained by

$$\mu_{n,p} = v_{n,p}/E = d^2/t_{n,p} V_0 \quad (4)$$

where V_0 is the applied voltage.

At higher initial concentrations of charge carriers distortion of the linear decay can originate from space charge build-up. Especially if the negative charge carriers are highly mobile electrons and the positive charge carriers are much less mobile ions, the decay of the electron current will be influenced by the space charge field originating from the positive ions.

If an electron scavenger is present, mobile electrons will be converted to slow ionic species so that the electron current decreases as the reaction proceeds. The time dependence of the current is given by

$$i_n(t) = i_n(0) e^{-k[S]t} \quad (5)$$

k the bimolecular rate constant and $[S]$ the scavenger concentration.

At low scavenger concentration $[S]$ or small rate constant k , neutralization of electrons at the anode is competing with scavenging. Measurements for the determination of k should be made in a concentration range where the condition

$$t_n > (k[S])^{-1}$$

is fulfilled.

2.2 Irradiation Conditions

Excess charge carriers were generated by ionizing the liquid with a pulse of x-rays from a 15 MeV linear accelerator. The pulse length was 5 to 10 nsec in the experiments with excess electrons while longer pulses (20 to 100 nsec) were used in experiments with positive excess charge carriers. The absorbed dose per pulse varied between 0.1 and 10 mrad, which corresponds to initial charge carrier concentrations of 2.5×10^7 to 2.5×10^9 cm⁻³ taking a value of $G(\text{free electron}) = 1$ ¹⁸. The dose was monitored with an air ionization chamber mounted

in the x-ray beam. Since the observed current is proportional to the number of charge carriers present in the volume, the initial electron concentration n can be calculated from

$$i_n(0) = n e \mu_n (V/d) F, \quad (6)$$

F = electrode area.

Thus, through extrapolation of the linearly decaying electron current, both μ_n and n may be obtained simultaneously.

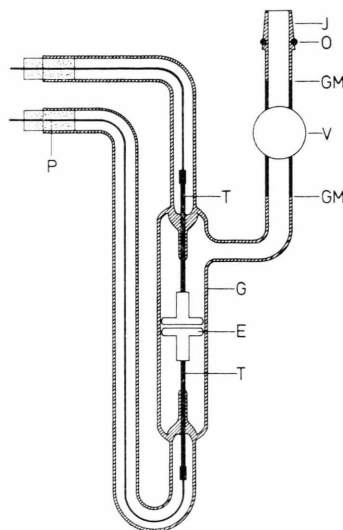


Fig. 1. Measurement Cell: J, 14/20 standard taper joint; O, Viton O-ring; GM, Glass-Metal seals; V, Hoke Series 480 Bellows Seal valve; T, Tungsten lead; E, Electrode; G, Pyrex-Glass; P, Rubber Plug.

One of the measurement cells used is shown in Figure 1. It was comprised of two circular flat electrodes (15 mm diameter) made of aluminum or stainless steel enclosed in a pyrex glass envelope. The electrode separation for each cell was measured accurately with a kathetometer. The leads to the electrodes were enclosed in pyrex glass tubes. The cell was immersed into a bath of a liquid coolant suitable for the desired temperature. Temperatures between the melting point and the boiling point of liquid methane were obtained with a liquid methane bath and for temperatures above the boiling point 2-methylbutane or a mixture of n-butane and isobutane were used as coolants. The desired temperature was obtained by cooling the bath with liquid nitrogen and the constancy of the temperature was monitored. For some experiments a simple automatic cryostat was used which pumped liquid nitro-

gen through a copper tube immersed in the bath. The temperature could be held constant to about ± 2 degrees. The cell was sealed with a metal bellows valve so that the liquid stood under its own vapor pressure. The measurements were carried out with several cells having different electrode spacings.

2.3 Sample Preparation

Methane of 99.995 Vol.-% purity as supplied by Messer Griesheim GmbH was passed through traps of activated silica gel and charcoal. The charcoal trap consisted of a quartz tube filled with charcoal (Merck, Darmstadt) which was activated by heating it to 600 °C and pumping on it for at least two days with a high vacuum line. The silica gel was in a pyrex U tube, heated up to 300 °C and also connected to the high vacuum line. Activation was completed when the pressure dropped below 1×10^{-3} with the traps hot. The traps and the methane gas tank were then cooled to -78 °C with dry ice before the methane was passed through the traps into an evacuated bottle with freshly activated silica gel. The bottle was connected to a high vacuum line and the purified methane was stored at liquid nitrogen temperature.

The measurement cell was evacuated to 10^{-5} to 10^{-6} torr, flushed with gaseous methane several times and filled by transferring the purified methane via vacuum distillation.

For the scavenger experiments the cell was filled with oxygen of a defined partial pressure, cooled to liquid nitrogen temperature and the methane was added by condensation under a methane pressure of 200 torr. Measurements were carried out for oxygen concentrations from 1.1 to 17.2 $\mu\text{moles/l}$.

2.4 Current Measurements

The electrical circuit was similar to the one already described by SCHMIDT and ALLEN¹⁵. The measurement cell was connected to a fast amplifier (Keithley Mod. 111 input 10 M Ω , output 50 Ω , amplification $\times 1$) with a short coaxial cable of $C_c = 25$ pF capacity. The input of the amplifier was shunted by a resistor R , so that the time constant RC was small compared to the time of the decay. Usually 1 K Ω to 50 Ω were employed. The signal could be amplified further by a maximal factor of 100 by two Keithley amplifiers Mod. 109, input, output 50 Ω , amplification $\times 10$. The cell and the amplifiers were placed in an electrically double shielded cabin near the target of the accelerator. The X-ray beam was collimated by lead bricks to a cross section of about 1.5×5 cm² and the cell was positioned in this area.

The signal and the voltage applied to the cell were transmitted via double shielded coaxial cables. The oscilloscope, (Tektronix Mod. 585 A with an 82 or 1A5 plug-in), and the power supply were housed in a Faraday cage which was connected to the outer shield.

For the measurements of the ionic mobilities the cell was connected directly to the signal cable which was fed into a sensitive dc-amplifier (Tektronix, Type 1A7A) with a $1\text{ k}\Omega$ resistor across the input. The time constant was of the order of $10\text{ }\mu\text{sec}$, much less than the shortest drift time observed.

In the scavenger experiments doses of 10 to 100 mrad per 5–10 nsec pulse were applied and the decay of the electron current was registered at low field strength (100 V/cm). Higher field strengths were used at higher O_2 concentrations to improve the signal/noise ratio with care taken that the electron half-life with respect to scavenging was much less than the drift time.

3. Results

For the determination of the mobility the drift velocity at various applied electric fields was measured. Figure 2 shows two oscillograms of the electronic and the ionic component of the ionization current after the pulse. From these traces t_n and t_p and the drift velocities were obtained. In Fig. 3 the electron drift velocity at various field strengths is plotted. Many experiments with different cells and different liquid samples were carried-out and the

points plotted are the average values at each field strength. At very low field strength the decay is not linear in time and the pertinent time constant is determined either by the reaction of the electrons with residual impurities or by the positive space charge. At higher field strength the drift time to the electrodes is shorter than the half-life with respect to impurity reaction and therefore t_n^{-1} or v_n is proportional to E . Above 1.5 kV/cm , the drift velocity seems to grow proportional to \sqrt{E} . From the dependence $v_n = \mu E$, the mobility is obtained. The value at $T = 111^\circ\text{K}$ (the boiling point of liquid methane) is $\mu_n = (400 \pm 50)\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ somewhat lower than previously reported in our preliminary communication³¹. The present value is the average of many measurements with cells of different electrode separation and using improved purification techniques so that the proportionality region could be extended to lower field strengths. In Fig. 4 mobility values at different temperature are given. The liquid was under its own vapor pressure. In contrast to other hydrocarbon liquids the mobility increases with decreasing temperature in liquid methane.

Evaluation of the ionic part of the ionization current yielded a drift velocity which was proportional to the electric field up to the highest field strength applied. Figure 5 shows the results obtained at three different temperatures and in Fig. 6 the data are represented in an Arrhenius plot.

The addition of oxygen to the liquid methane changed the decay of the electronic part of the ioni-

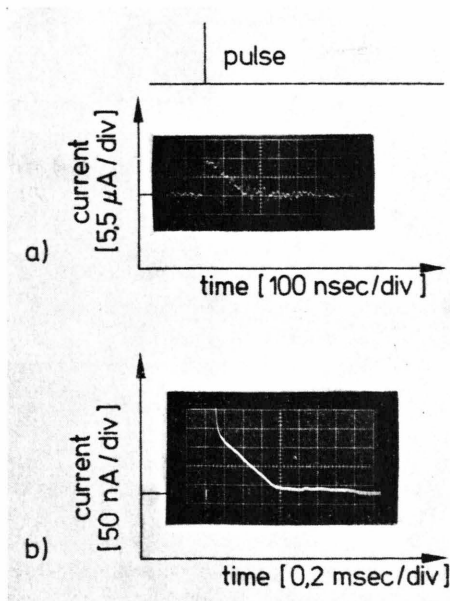


Fig. 2. Decay of the ionization current; a) Electron current, $E = 890\text{ V cm}^{-1}$, 5 nsec pulse; b) Ion current, $E = 44.5\text{ kV cm}^{-1}$, 100 nsec pulse.

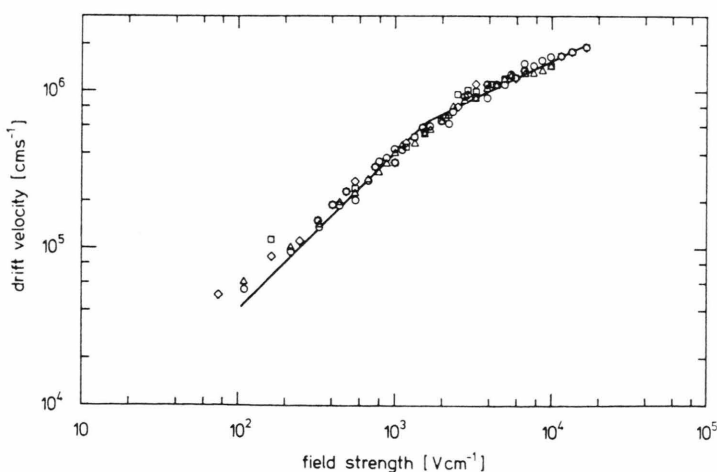


Fig. 3. Dependence of electron drift velocity on electric field strength in liquid methane at $T = 111^\circ\text{K}$, 1 atm, \square , \circ , \triangle , \diamond different cells and fillings.

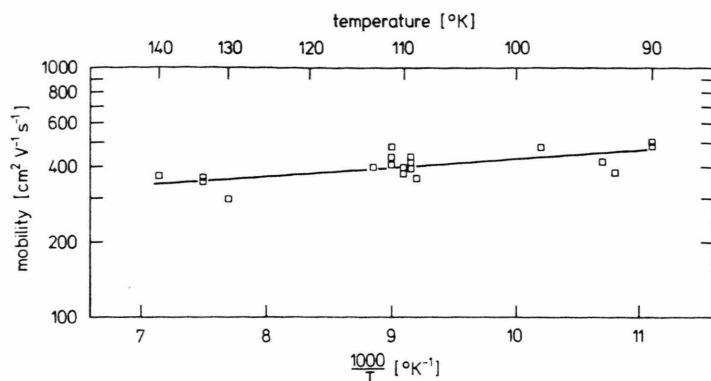


Fig. 4. Temperature dependence of the electron mobility in liquid methane.

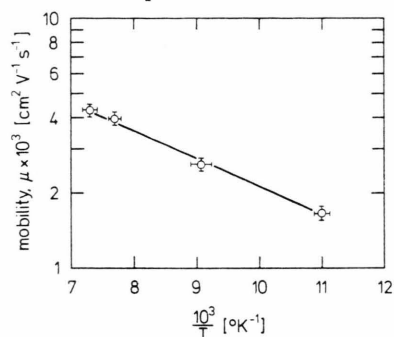


Fig. 6. Arrhenius plot of the positive charge carrier mobility.

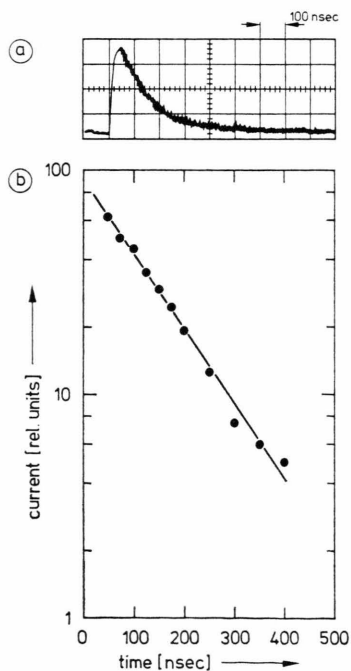


Fig. 7. a) Decay of the electron current due to reaction of electrons with oxygen; $[O_2] = 11.1 \mu\text{mole/l}$, $E = 222 \text{ V cm}^{-1}$. b) First order plot of trace a).

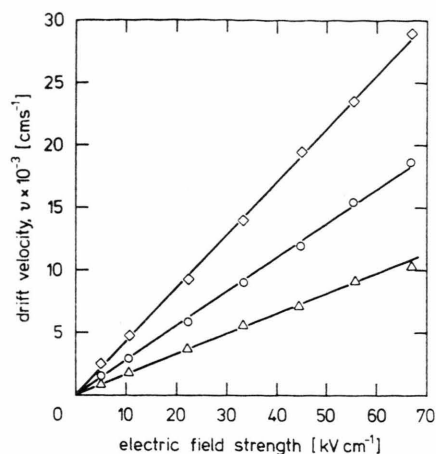


Fig. 5. Dependence of the drift velocity of the positive charge carrier on the electric field strength in liquid methane at three different temperatures; \triangle 91 °K, \circ 110 °K, \diamond 137 °K.

zation current from linear to exponential. The concentration of the oxygen had to be high enough so that the decay time was less than the drift time of the electrons at the particular field strength. Figure 7 a shows an oscillogram of the electron current i_n and in Fig. 7 b $\ln i_n$ versus time is plotted. The kinetics of the decay is pseudo-first-order and in Fig. 8 the apparent rate constant as a function of the

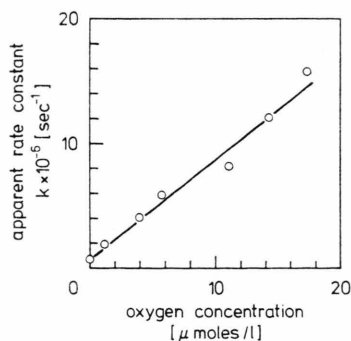


Fig. 8. Apparent rate constant $k_{ap} = k[S]$ as a function of the oxygen concentration.

oxygen concentration is shown. From the slope a bimolecular rate constant of $k_{O_2} = 8.4 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ for the reaction



at $T = 109 \text{ °K}$ is obtained.

4. Discussion

4.1 Electron mobility

Direct measurements of excess electron mobilities in highly purified hydrocarbons have become possible only quite recently. The data obtained so far can be summarized in the following points:

1. The electron mobility in liquid hydrocarbons is strongly affected by the molecular structure with the branched isomers exhibiting greater mobilities than their straight chain analogue.

2. In all the hydrocarbons investigated thus far the electron mobility shows a positive temperature coefficient which is greater the smaller the mobility.

3. The drift velocity remains proportional to the electric field up to the highest field studied (e.g. 140 kV cm^{-1} in n-pentane and 15 kV cm^{-1} in neopentane). In tetramethyl silane the drift velocity exceeds 10^6 cm s^{-1} at 15 kV cm^{-1} , a value greater than the limiting electron velocity in liquid argon, krypton, or xenon.

4. The electron motion in pure liquid hydrocarbons and in binary mixtures can be described by a trapping model leading to a dependence of the mobility on the temperature of the form

$$\mu_n(T) = (\mu_t/\nu \tau_0) \exp\{-E/RT\}. \quad (7)$$

Here μ_{tn} is the mobility of the electron in the quasi-free state, τ is the time of residence in the trap and E is the activation energy for promoting an electron from the trapped state to the quasi-free state. ν is the jump frequency. The trap is assumed to be formed by several molecules.

The quasi-free electron state in a dielectric liquid can be described as a plane wave which is scattered by single atoms^{32, 33} or molecules²². DAVIS, SCHMIDT, and MINDAY demonstrated that μ_{tn} of neopentane, n-hexane and their binary mixtures can be calculated from their modification of the Cohen-Lekner theory. They obtained a value of $\mu_{tn} \approx 150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for both neopentane and n-hexane²³. This value also was obtained from the extrapolation of the temperature dependence of the electron mobilities in various hydrocarbons to infinite temperature¹⁷. A similar result was obtained by FUEKI et al.³⁴ who estimated μ_{tn} for various hydrocarbons from the Cohen-Lekner theory.

However, thus far no investigation on the temperature dependence of μ_{tn} in these liquids has been made. According to the Cohen-Lekner theory μ_{tn}

should vary with temperature as $T^{-3/2}$. Any such dependence would not show up, however, in the measurement of the temperature dependence of the electron mobility at low fields, since the exponential dependence on T is the dominating factor in Equation 7.

The results obtained for liquid methane show some interesting features which shall be listed for comparison:

1. The electron drift velocity at lower field strengths up to 1.5 kV cm^{-1} is proportional to the electric field and the mobility obtained is $\mu_n = (400 \pm 50) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 111° K .

2. Above 1.5 kV cm^{-1} or for drift velocities greater than $6 \times 10^5 \text{ cm s}^{-1}$ the mobility becomes field strength dependent and the drift velocity varies with \sqrt{E} . The transition occurs at a velocity which is about 5 times the velocity of sound in liquid methane at that temperature ($v_s = 1.41 \times 10^5 \text{ cm s}^{-1}$).

3. The mobility shows a negative temperature coefficient, although the data seem to follow an $e^{6/T}$ dependence rather than a dependence on $T^{-3/2}$.

These observations are consistent with a model depicting the electrons moving through a dense packing of molecules. At low field strengths the thermal velocity v_{th} of the electrons is much greater than the drift velocity and the energy distribution is Maxwellian. At higher field strength the field energy of the electrons increases and becomes comparable or greater than kT . A \sqrt{E} dependence of the drift velocity follows and also the dependence of μ on $T^{-3/2}$ is implied if the mean free path λ varies with T^{-1} .

The more rigorous treatment by Cohen and Lekner gives for the electron mobility in the quasi-free state

$$\mu_{tn} = \frac{2e}{3n} \left(\frac{2}{\pi m k T} \right)^{1/2} [4\pi a^2 S(0)]^{-1}; \quad (8)$$

e electron charge, m electron mass, n number density of liquid methane, k Boltzmann constant, T absolute temperature, a scattering length, $S(0)$ structure factor with

$$S(0) = n k T \chi_T \quad (9)$$

χ_T isothermal compressibility.

Since we measured μ_{tn} in liquid methane and the other values are available, we can estimate the scattering length, a , and the scattering cross section for electrons, $\sigma_1 = 4\pi a^2$. The isothermal compressibility

was obtained by using an equation derived by YOSIM³⁵ for fluids of rigid spheres which relates χ_T with the thermal expansivity and the hard core diameter. With $\chi_T = 1.3 \times 10^{-10} \text{ cm}^2 \text{ dyne}^{-1}$ we obtained $a = 0.86 \times 10^{-8} \text{ cm}$ and $\sigma_1 = 1.6 \times 10^{-15} \text{ cm}^2$.

The scattering cross section in gaseous methane varies from 10^{-15} cm^2 for $3 \times 10^{-2} \text{ eV}$ to 10^{-16} cm^2 for $3 \times 10^{-1} \text{ eV}$ electrons³⁶.

The energy ϵ_0 to inject an electron from the vacuum into the quasifree state in liquid methane was estimated to be $\epsilon_0 = -1 \text{ eV}$ by applying a semi-empirical relation developed by FUEKI et al.³⁴. This value follows the empirical correlation between the electron mobility and ϵ_0 which has been found by HOLROYD and ALLEN³⁷.

From Eq. (8) we can estimate the mobility μ_{fn} in the quasi free state at room temperature by

$$\mu_{fn} = \left(\frac{295}{111} \right)^{-3/2} \mu_{fn} (\text{liquid methane}) \quad (10)$$

which yields $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, in reasonable agreement with the value of $150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ quoted above.

4.2 Electron Scavenging

Observation of highly mobile electrons in hydrocarbon liquids is obscured by their rapid reaction with impurities present. A very prominent electron scavenger is oxygen and extensive degassing procedures are necessary before drift velocity measurements are possible. From our measurements a bimolecular rate constant for the reaction of excess electrons in liquid methane at $T = 109^\circ \text{K}$ with oxygen of $k = 8.4 \times 10^{11} \text{ l mole}^{-1} \text{ s}^{-1}$ was obtained. Recently several investigations were published in which electron scavenging in various hydrocarbons was studied either by optical or conductometric detection techniques^{20, 38, 39}. Generally, the bimolecular rate constant k for the reaction



was found to range from $10^{10} - 10^{13} \text{ l mole}^{-1} \text{ s}^{-1}$.

4.3 Positive Charge Carriers

The slow charge carrier observed in liquid methane has a mobility which is $\sim 10^5$ less than the electron mobility. Since these drift velocity measurements were carried out at comparatively high field strengths, all electrons should be swept-out of the

sensitive volume of the measurement cell before they had time to react with impurities and thus be converted to negative ions with a similar low mobility. Furthermore, the linear decay of the electron current at lower field strengths indicates that no attachment occurred. We can assume, therefore, that the observed slow carrier is a positive species.

The temperature dependence of the mobility can be described by an Arrhenius equation and on the other hand the mobility varies inversely proportional to the viscosity meaning that Walden's rule applies. This then leads us to expect that Stokes law should be applicable to the methane ion. Inserting a hard core radius of $r = 1.9 \text{ \AA}$ ⁴⁰ Eq. (11)

$$\mu_p = e/6\pi\eta r \quad (11)$$

yields the mobilities listed in Table 1. The calculated mobilities are approximately 40% greater than the observed values, which implies that polarization

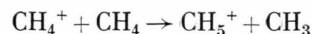
Table 1. Temperature dependence of positive charge carrier mobility and liquid methane viscosity.

T [°K]	η (a) (c poise)	$\mu_p (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \times 10^3$	
		observed	calculated
91	0.203	1.6	2.2
110	0.122	2.7	3.7
137	0.068 (b)	4.3	6.6

(a) from V. J. JOHNSON, A Compendium of the Properties of Materials at Low Temperature, Part I, WADD Techn. Rep. 60-56 (1960).

(b) extrapolated value.

interaction of ion and liquid molecules leads to an increase of the apparent radius. On the other hand the nature of the positive charge carrier is not known. It is possible that CH_4^+ is the species which we observe although the reaction



is thought to occur in liquid phase radiolysis⁴¹. In liquefied rare gases the diatomic ion is formed²⁸.

We have to point out that the positive species are observed several hundred microseconds after their generation by a pulse of X-rays. It is possible that in the early stages of their life-time the positive parent charge carriers exhibit a greater mobility until they undergo a transition either by transferring the charge to an impurity with a lower ionization potential or by converting into another species. From our present results we cannot obtain unambiguous information on the nature of the positive species.

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