Drift Mobilities and Conduction Band Energies of Excess Electrons in Dielectric Liquids

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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

E. Ambler.

ERNEST AMBLER, *Acting Director*

Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or G values (molecules formed or destroyed per 100 eV). Various indirect methods based on G values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

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The properties of electrons in liquids which are covered in this review include drift mobilities and the energy level (V_0) at the base of the conduction band. Tables are given of zero–field electron mobilities for several liquefied diatomic and inert gases, a number of aliphatic and aromatic hydrocarcarbons, and polar solvents. V_0 values are given for liquid helium and argon, a number of hydrocarbons, tetramethylsilane and tetramethyltin. Theories attempting to explain these results are described in a qualitative way.

Keywords: Conduction band; drift mobility; energy levels; excess electrons; hydrocarbons; ion mobility; liquids; mobility; quasifree electrons; solvated electrons.

1. Introduction

Modern views on the nature of matter arose from experiments on electrical conduction in gases, which led to the discovery of the electron as a constituent particle of all substances. Application of the electron concepts to electrical conduction in solids then led to such advances that the majority of all physicists now devote themselves to solid state studies. Though such great results have followed from studies of electrons in gases and solids, little work on electrons in liquids has been done until very recent years. Experiments at the University of Chicago on electrons in liquid helium and argon, and their remarkably successful theoretical interpretation, have in the last seven or eight years stimulated work at other laboratories on a variety of other liquids. Much of this work has been motivated by desire to obtain better basic understanding of effects of radiation on materials and biological organisms.

The most significant, readily measurable properties of the electron in a medium are its drift mobility, and the energy level of the conduction electrons. This publication summarizes data on these topics.

2. Definitions

An electron or ion, accelerated in a fluid medium by an electric field E, quickly attains a terminal velocity v (when the frictional force balances the electrical force) which is proportional to the field, if the field is not too large:

$$v = \mu E \tag{1}$$

The mobility μ is always given in cm/s per volt/cm, or $cm^2V^{-1}s^{-1}$. Values of μ are characteristic of the charged species and the medium. The mobility of an electron or singly–charged ion is related to the diffusion coefficient D by the Nernst equation

$$\mu = De/kT \tag{2}$$

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where e is the electronic charge, k Boltzmann's constant and T the absolute temperature.

Under steady–state conditions with a constant applied field, the amount of positive charge reaching the cathode per unit time must equal the amount of negative charge reaching the anode. Then the total current density in unit field (in units of ions per second per cm^2) is

$$i/E = \sum_n c_n z_n \mu_n + \sum_p c_p z_p \mu_p \tag{3}$$

where the subscripts refer to negative and positive charge carriers, c is concentration in ions per cm^3, z is the number of electron charges on each ion (unity in all cases considered here) and the two sums are equal. The current density I in amperes per cm^2 is related to i by $i = IN/F = I \cdot 6.24 \times 10^{18}$ where N is Avogadro's number and F is the Faraday constant. The ratio I/E is the *conductivity* σ; if E is in volts/cm, σ is given in ohm^{-1}cm^{-1}.

However, under different conditions, the physical systems governed by this equation may be quite different. In electrolyte solutions, the applied field is always relatively small, and the concentration of ions so large ($c > 10^{15}$) that a small fractional excess of ions of one sign would lead to an internal field large compared to the applied field, so this excess charge would neutralize itself by diffusion. Hence in the physical chemistry of electrolyte solutions, the maintenance of electrical neutrality in all macroscopic volumes is assumed. The conductivity of the solution per g–equivalent of total electrolyte per cm^3 (extrapolated to zero concentration) is called Λ_o:

$$\Lambda_o = \sigma N/\Sigma cz = Fi/E\Sigma cz \tag{4}$$

where Σcz is the total number of unit charges of either sign per cm^3. Λ_o is the sum of equivalent conductances of each individual ion present, weighted by their respective relative concentrations:

$$\Lambda_o = \sum_n \lambda_n c_n/\Sigma cz + \sum_p \lambda_p c_p/\Sigma cz \tag{5}$$

Comparing eqs (4) and (5) with eq (3), we see that

$$\lambda = F\mu = 96500\ \mu \tag{6}$$

if as usual λ is given in cm^{2}ohm^{-1}g–equiv^{-1} and μ in cm^{2}V^{-1}s^{-1}. This equation is used in determining the mobility of solvated electrons.

In an ionization chamber, as used to determine the dose rate from ambient γ– or X–rays, the situation is quite different. Here the field is kept high so that ions are swept out of the chamber as fast as formed. The positive and negative ions have concentration gradients in opposite directions, and the mean concentration of each ion varies inversely with its mobility; so with parallel plates electrical neutrality exists only at one plane in the chamber. It is still true under constant irradiation, that at the steady state half the current is carried by positive charges and half by negative; but the time required to attain this state after any change in conditions is the time for the slowest ion to traverse the entire width of the chamber. Drift time determinations for highly mobile electrons are made under conditions resembling those of the ion chamber.

The states available to an electron in a liquid resemble those in a solid, and fall into two classes: *localized* and *delocalized*. The delocalized state is that of a conduction electron in a metal or semiconductor, or an electron moving through a dilute gas; such electrons are often called *quasifree*. Only an electron in a vacuum is really free; the motion of the quasifree electron is limited by scattering from gas molecules, or (in crystals) from lattice imperfections or irregularities due to thermal motions (phonon scattering). That existence of delocalized states in condensed matter does not depend on long–range crystalline order is proved by the simple fact that liquid mercury is a good conductor. In most non–metallic liquids, electrons introduced by ionization (or by photodetachment from immersed metal surfaces) enter the delocalized conduction state and will remain there if the electrical potential field within the liquid is reasonably regular. Monatomic liquids (argon) and those polyatomics having molecules of nearly spherical symmetry (neopentane) provide the most regularly varying potentials.

Anisotropy of the molecular polarizability and the presence of permanent dipoles in the liquid create stronger irregularities which break up the electron wave and cause the electrons to become localized at the points of lowest potential. In a solid crystal or glass, these electrons are said to be *trapped*, and do not contribute to the conductivity. In a liquid, the electrons are said to be *solvated*, and the whole complex of electron and trapping molecules can move in an electric field and exhibit conductivity; but its mobility is orders of magnitude less that that of a quasifree electron, and is similar to that of ordinary molecular ions. The mobility of the quasifree electron normally decreases with increasing temperature, because of increased phonon scattering; but the mobility of a solvated electron like that of a molecular ion depends largely on the fluidity of the medium and increases with increasing temperature.

The energy level of a quasifree electron in a liquid, relative to a free electron in the vacuum, is called V_0, and is always given in electron volts. For a given liquid, V_0 increases with density and therefore decreases with rising temperature. The exchange forces tend to repel the electron from the molecules of the liquid, but the electron also induces dipoles in the molecules by polarization, which tend to attract the electron. The greater the attraction compared to the repulsion, the more negative is V_0. In liquid helium, the polarizability is low and V_0 is distinctly positive. An electron formed by ionization in this liquid repels the atoms of the liquid and forces about itself a region of reduced density, the behavior of which can be closely approximated by assuming the electron to be enclosed by a bubble with a sharp boundary, containing no helium. The mobility of such a "bubble" is very close to that of a molecular ion, like that of a solvated electron; but the nature of these three negatively charged entities is thought to be entirely different.

Liquid hydrocarbons exhibit a wide range of electron mobilities lying between those of quasifree and solvated electrons. It is thought that the traps in these liquids hold electrons less firmly than those in polar liquids, so that diffusion of electrons from trap to trap is possible. Two mechanisms are proposed for this passage. In one model, the electrons are in shallow traps having energies not far below the conduction band, so that a thermodynamic equilibrium exists between solvated and quasifree states. On this model, the observed mobility is given by the quasifree mobility, multiplied by the quasifree equilbrium fraction, which increases with temperature. For the other model, we note that quantum mechanics allows an electron, retained in a certain energy state by a potential barrier, to leak through the barrier, provided a state of matching energy exists for the electron on the other side of the barrier. In general, a potential trap in a liquid, adjacent to a solvated or trapped electron, is not likely to be of the right size to provide the energy match that will make leakage possible; but thermal agitation continually alters the shape of the traps, so that the higher the temperature the more frequently the energy match will occur. This model is called *phonon–assisted–hopping*, or simply hopping.

The bubble model, hopping model and passage through the conduction band lead to similar phenomenological predictions. Perhaps the future will provide a more comprehensive theory for cases in which the electron is neither firmly solvated nor entirely "quasifree".

3. Methods of Measurement

3.1. Electron Mobilities in Non–Polar Liquids

Measurements of drift times in work reported here have involved electron lifetimes of at least several microseconds. Extremely high purity of the liquid is then required with respect to electron–attaching impurities. If the rate constant for the electron–impurity reaction is 10^{13} $M^{-1}s^{-1}$ (not unusually high) and a mean electron lifetime of 10^{-5}s is required for the measurement, the concentration of reactive impurity should be kept below $10^{-8}M$.

Given sufficient purity, the *double–shutter method* is the most direct and accurate [660394].[1] Electrons formed at a cathode, usually by ionization, drift to a collecting anode, while retarding potentials are periodically applied to a pair of double grids, acting as gates, located in the drift space. The current reaches a maximum when the time to drift between the grids is a multiple of the period between openings of the gates. By this method, electron mobilities in liquid argon have been measured with an accuracy of ±1.5% [719353].

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[1] Numbers in brackets indicate the references at the end of this paper.

Alternatively a single grid near the cathode can be pulsed; or, if the electrons are generated by illuminating the cathode with ultraviolet light, the period is obtained by winking the light on and off with a shutter (single shutter method) [729022].

A simpler method (thin layer method), used for tetramethylsilane [700140] is simply to turn on X–rays, which pass through the solution only in the vicinity of the cathodes, and note the time required for the current to reach its maximum, which is the drift time across the cell. In the "thick layer method" [731036] the entire cell is irradiated with a very short pulse of X–rays. As the ions are pulled out by the field, the current decreases linearly with time, reaching zero at the drift time.

The Hudson method [460003] has proved useful for measuring electron mobilities in hydrocarbons [700140]. When X–rays are turned on, irradiating uniformly the entire volume between cathode and anode, the current rises parabolically with time to a maximum value, the time to maximum being the drift time of electrons across the cell. The rise of the electron current is followed by the much slower rise of the positive ion current. Impurities distort the electron rise curve and tend to give too high mobility values; a method of correcting for the impurities has been devised [741036].

All the above methods require the use of extremely small electron currents in order to avoid space charge effects, with corresponding care to avoid spurious readings in the electrical measurements.

Judging by consistency of the results when applied to hydrocarbons, the thin layer, thick layer and Hudson methods are subject to errors of about ±10%. However, the shutter methods do not seem to have given much better results with hexane, and the difficulties in obtaining higher accuracy with hydrocarbons may lie more in impurity effects than in the physical methods used.

A less direct method, which entails less strict purity requirements, is used at laboratories which have pulse radiolysis setups with nanosecond resolution times. Conductivity is measured after a known pulse of radiation, much more intense than used in the drift time methods, and the decay of the current is usually largely due to ion recombination. In liquids such as hydrocarbons, where the electron mobility is hundreds of times greater than that of the positive ions, the current is fixed essentially by the product of the electron concentration and mobility; if the electron yield is known by other measurements, and the absolute dose has been accurately determined, extrapolation of the current back in time to the end of the radiation pulse allows the mobility to be calculated. Uncertainties as great as 30% in the value of the free–ion yields make this method less accurate as a measure of mobility than the drift–time determinations.

3.2. Mobilities of Solvated Electrons

The pulse conductivity method has been used to determine the mobility of solvated electrons in water. The concentration of the electron is determined optically, simultaneously with the conductivity. As the electron disappears, it is replaced in the solution by the OH^- ion; the change in conductivity measures the difference in mobility of e^- and OH^-, which turns out to be surprisingly small. Similar methods have been used for other polar liquids [720153]; but the mobility of other ions in these solvents is less well known than in water, so these results are presumably less accurate.

Ammonia dissolves alkali metals such as Na to form stable solutions. The extrapolated conductivity $\Lambda_0 = \lambda(e^-) + \lambda(Na^+)$, and a transference number experiment has given the mobility of e^- in this solvent. The stability of the electron thus allows the mobility to be determined by purely 19th–century methods.

3.3. Conduction Band Energies

Conduction band energies are measured by noting the difference in work function of a metal in vacuum and immersed in the liquid. The logarithm of the photoelectric current emitted from a metal illuminated at different wavelengths in the ultraviolet and visible is plotted against the quantum energy of the light, showing a curve (Fowler function) which rises rapidly when the energy exceeds a certain value, the *work function*, characteristic of the metal. Liquid is distilled onto the metal, and the experiment repeated; the same shape curve is found, but is shifted along the energy scale to give a different value of the work function. The electrons initially go into the conduction band of the liquid, so the change in the work function is equal to V_0. After the liquid measurement, the liquid is distilled out and the vacuum measurement repeated to make sure no change has occurred in the metal surface to affect the work function; clean hydrocarbons do not affect the surface.

Relative values of V_0 for different liquids are also obtained by determining photoionization thresholds in different liquids, using solutions of a readily ionized solute such as TMPD (tetramethylphenylenediamine). Photoionization shifts from one liquid to another were found to be equal to photoelectric work–function differences between the same liquids [747297]. These determinations are not sensitive to the presence of electron–attaching impurities, even at concentrations as high as $10^{-3}M$.

4. Data on Electron Mobilities

4.1. Elements and Diatomic Gases

Electron or negative ion mobilities μ_- in some liquefied monatomic and diatomic gases, and in liquid sulfur are shown in table 1. All these data were obtained by some version of the double– or single–shutter methods. Some data on solids are included to show the behavior of μ_- on melting.

The bubble model for the electron in liquid helium [658008, 658009] is now generally accepted (see for example [730316]). Above the λ point (2.2 K) the mobility varies approximately inversely with the viscosity; but at lower temperatures, though the viscosity vanishes there is no discontinuity in the mobility; it rises (fig. 1) from 0.033 at 2.2 K to 220 at 0.5 K, and at lower temperatures is proportional to T^{-3}; $\mu T^3 = 27.64\ K^3\ cm^2\ V^{-1}\ s^{-1}$ ($T < 0.5$ K), according to [729251] which presumably supersedes an earlier publication [680854] by the same author. These results have led to some new insights on superfluid behavior.

In liquid neon, as in helium, the electron mobility is close to that of the positive ion. In solid neon, however, the electron mobility is many orders of magnitude larger, and is close to that of solid argon; but in argon, krypton and xenon the mobility falls only by a factor of 2 on melting. The difference is that electrons injected into the solid are expected to remain in the conduction band, even though the

TABLE 1. Zero–field mobility of electrons (or negative ions) in condensed phases of elements and diatomic gases

Substance	State	μ_- $cm^2V^{-1}s^{-1}$	T, K	Temp. effect, equation	Temp. range, K	Reference
He	liq.	0.020	4.2	See fig. 1	0.274–5.18	620159, 600073, 729251
Ne	solid	600.	25.	—	—	720839
	liq.	0.0016	25.5	$\mu_- = 3.0 \times 10^{-4}T + 0.0070$	26–31	720839
	liq.	0.0008	25.5	$\ln(\mu_-T) - 2.03 - (151/T)$	25.5–43	729075
Ar	solid	1000	82	—	—	689006
	liq.	475	85	—	—	689006
	liq.	470	90.1	See fig. 2	90–160	660394, 719353
Kr	solid	3700	113	—	—	689006
	liq.	1800	117	—	—	689006
	liq.	1300	120	See fig. 5	120–180	660394
Xe	solid	4500	157	—	—	689006
	liq.	2200	163	—	—	689006
		1080	167	See fig. 6	167–315	741134
N_2[a]	solid	0.0017	63	—	—	720840
	liq.	0.00065	63	$\mu_- = 3.57 \times 10^{-5}T - 0.00160$	63–77	720840
O_2[a]	liq.	0.00045	62	$\mu_- = 3.70 \times 10^{-5}T - 0.00185$	62–89	720840
CO[a]	solid	0.003	68	—	—	720840
	liq.	0.00087	69	$\mu_- = 4.78 \times 10^{-5}T - 0.00242$	69–78	720840
H_2[a]	liq.	0.0086	21	—	—	638002
Sulfur[a]	liq.	0.000100	393	$E_{activn.} = 0.15 \pm 0.02$ eV	393–433	687280

[a] Interpretation of these data as electronic rather than ionic mobilities is quite doubtful; see text.

repulsive terms lead to a highly positive V_0; but in the liquid, the atoms are free to move away from the electron and form the low–mobility "bubble". The bubble will be stable when V_0 is larger than the sum of energy terms required to form the bubble (pressure, surface tension and electrostatic forces). Before the mobility measurements were made, Miyakawa and Dexter [699050] calculated V_0 for neon by two methods, and concluded that the electron in a bubble should be only slightly more stable than in the conduction band. If this is true, application of a few hundred atmospheres pressure should collapse the bubble and cause a dramatic increase in the mobility; but this experiment has not been tried.

The electron mobility in liquid argon has been examined in great detail both experimentally and theoretically (figs. 2–4). Lekner [670446] calculated the drift velocity of electrons in liquid argon for a temperature near the melting point (84 K) using methods developed for explaining the conductivity of semiconductors, but calculating the potentials within the liquid from the atomic polarizability and electron scattering data for dilute argon gas. The final result gave the zero–field mobility of the liquid to within 5% of the experimental value, and also agrees extraordinarily well with the high–field electron velocity data, much of it obtained after the calculation was done (fig. 3). The levelling off of the velocity at the very highest fields studied was explained in a theory of Spear and Le Comber [690202]. Moreover, the decrease in mobility between 84 and 110 K follows the expected $T^{-2/3}$ law. Thus it may be said that the electron mobility in liquid argon up to 110 K is basically understood at least as well as any property of the liquid. At higher temperatures the mobility rises to a high maximum, with a sharp fall appearing just below the critical temperature (151 K) (fig. 2). The cause probably lies in changes of the electron's environment caused by microscopic density fluctuations that appear in the liquid as the critical

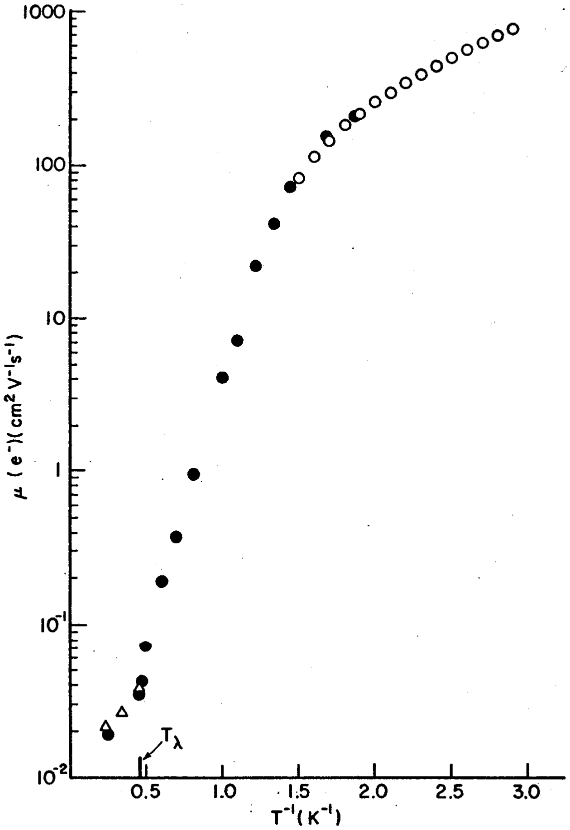

FIGURE 1. Mobility of electrons in liquid helium at pressures below 1 atm, plotted against recriprocal absolute temperature: open circles [729251]; closed circles [6000073]; open triangles [620159].

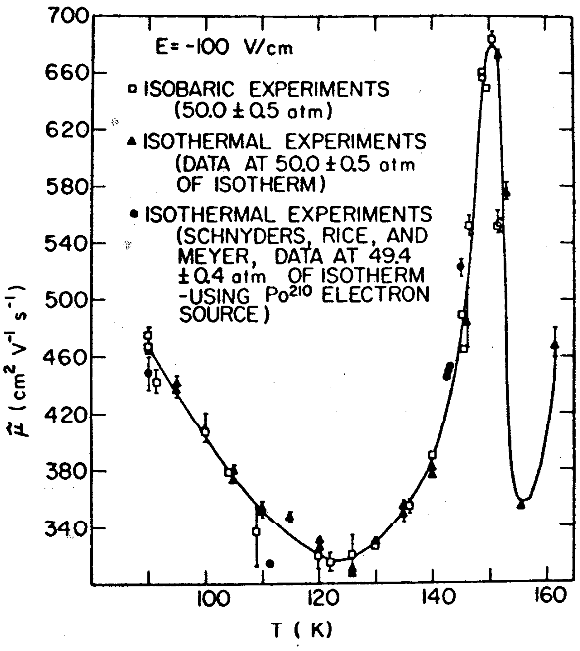

FIGURE 2. Comparison of apparent electron mobilities at −100 V/cm on a 50-atm isobar in liquid argon. Data from the isothermal experiments were obtained by taking the value at 50 atm from plots of apparent mobility versus pressure at constant temperature. Refer to [660394] for data obtained using a Po^{210} alpha-ray source. The figure shows the agreement between data using different sources and between data obtained through different thermodynamic routes. Figure from [719353].

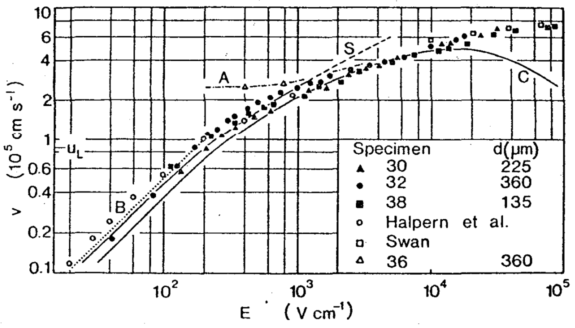

FIGURE 3. The field dependence of the electron drift velocity in liquid Ar at 85 K. Curve S, calculated from Shockley theory; curve C, theory of Cohen and Lekner; curve B is corrected for multiple scattering and also indicates the linear field dependence. Curve A: typical results from a speciment with short electron lifetime ($\simeq$ 200 ns). The sound velocity in the liquid is denoted by u_L. Figure from [689006].

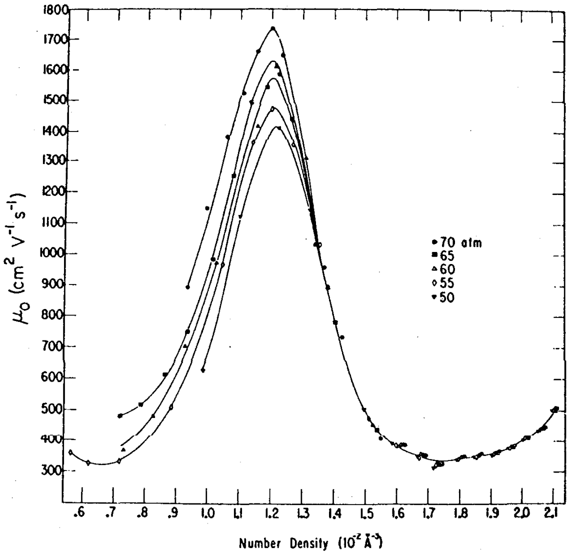

FIGURE 4. Zero-field electron mobilities as a function of number density in fluid argon. Figure from [719353].

temperature is approached. The treatment which was so successful at lower temperatures assumed the potential to be isotropic about the average position of each atom, which predicts that mobility should depend only on the liquid density. Figure 4, which summarizes the extensive and precise data of Jahnke, Meyer and Rice, shows that this is indeed true at the higher densities, but that at the higher temperatures the mobility for a given density is higher, the higher the pressure (and therefore the higher the temperature). Thus thermal fluctuations of the density lead to an increase in mobility, though it is not obvious that this should be so. Lekner [688043] pointed out that his calculated scattering length or square root of the scattering cross section for the electron in the liquid is positive, corresponding to scattering from repulsive centers, while in argon gas the scattering length is negative. At some intermediate density then the mean scattering length should be zero, and the mobility should fail to become infinite only because of fluctuations in the scattering process. It was to test the theory derived from this model that Jahnke carried out his extensive measurements. The results agreed with the theory in that the maxima at different pressures always occurred at temperatures such that the density was the same (0.0120 atoms/Å^3), and predicted the right shape for the mobility rise from the high–density side, but failed to explain other features of the data. Later, Jahnke, Holzwarth and Rice [728005] reported that no theoretical calculation of the scattering length could predict a zero at densities above the critical liquid density (0.0080 atoms/Å^3). Thus at present there is no good theory for the maximum in mobility below the critical temperature.

The mobility maximum also occurs in liquid krypton (fig. 5) and xenon (fig. 6). It is not known whether it exists in any of the many polyatomic liquids which have been studied, since measurements in these liquids have not been made sufficiently close to their critical temperatures.

Electron mobility increases with increasing density and polarizability in the series argon, krypton, xenon. The field dependence of the mobility sets in at lower fields in the higher atomic weight liquids, and the extrapolation to zero field is somewhat uncertain for xenon. In fact, Robinson and Freeman [741012] who looked at electron velocities in xenon by the maximum pulse current method, found that the velocity was proportional to the square root of the field, so extrapolation of μ to zero field would be impossible. However, their velocity figure was obtained by dividing the maximum conductivity by the free–ion yield, the value of which is perhaps somewhat dubious and is also field–dependent. More recently, Kimura and Freeman [741134] have published numbers obtained at fields of only 16 V/cm. Neither theory nor experiment has been applied as thoroughly to krypton and xenon as to argon. Since the theory of these cases, in which self–trapping is essentially absent, is basic to the understanding of

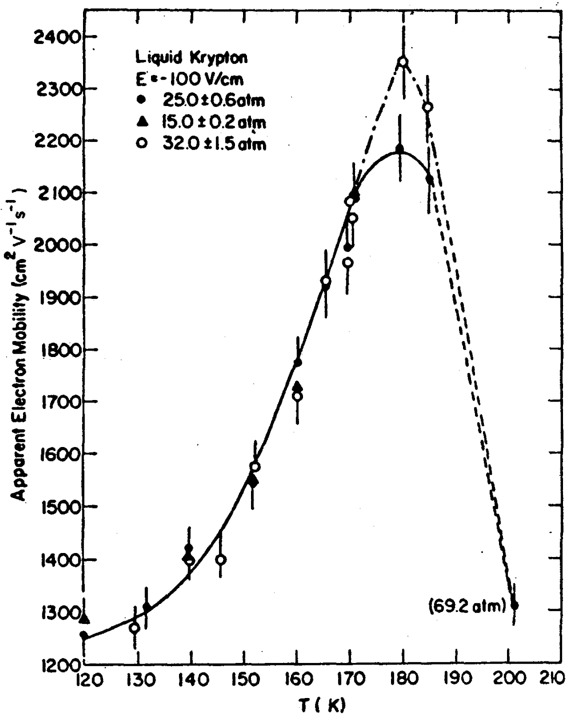

FIGURE 5. Apparent electron mobility in liquid krypton as a function of temperature. All points are measured at a constant electric field strength of −100 V/cm. Figure from [660394].

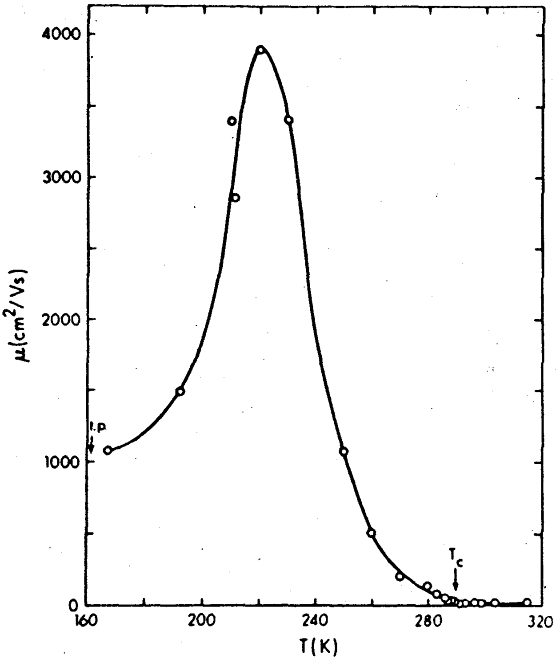

FIGURE 6. Apparent mobility of electrons in liquid xenon as a function of temperature. The pressure on the sample was the vapor pressure. Applied field strength = 16 V/cm. Triple point, t.p. = 161.3 K; critical temperature $T_c = 289.7$ K. Figure from [741134].

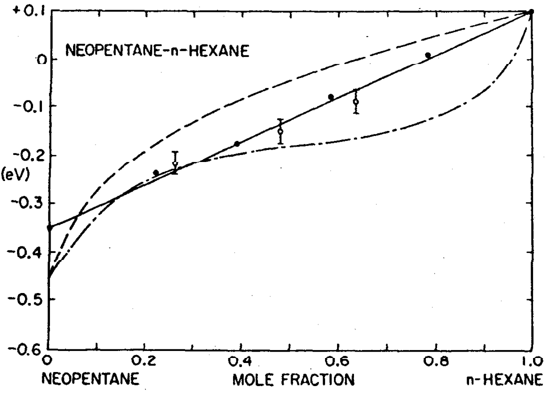

FIGURE 7. V_0 in electron volts *vs.* mole fraction hexane for neopentane-*n*-hexane mixtures; open points are from work function shifts of Zn; filled points are from TMPD photoionization threshold shifts; – – – –, bubble model prediction, [720242]; – · – · –, effective medium prediction, [738029]. Figure from [740079].

electrons in polyatomic liquids, in which widespread interest is now being shown, additional study of krypton and xenon would be desirable.

The other substances in table 1 all show much lower mobilities. Hydrogen was predicted by Miyakawa and Dexter [699050] to form "bubbles" about electrons, and the measured mobility, which lies between those of helium and neon, is consistent with this prediction. Oxygen gas (but not N_2 or CO) at reasonably high pressures reacts with electrons to form the ion O_2^-, and the negative species in liquid oxygen would be expected to exist in this form.

Mobile positive and negative species were seen in solid N_2 and CO, with μ 1–3 x 10^{-3} cm^2 V^{-1} s^{-1}, and in the low–temperature form of solid O_2 (36–44 K) but not in the high–temperature form (44–54 K). In liquid N_2 and CO, μ_- increased from about 0.8 x 10^{-3} to 1.3 x 10^{-3} cm^2 V^{-1} s^{-1} in the range from the melting point to 10° above it, in parallel with μ_+ and with the decrease in viscosity of the liquids. In sulfur similar phenomena were found, with μ_- falling by a factor of 25 to 1 x 10^{-4} on melting, then increasing at higher temperatures. At 160° C sulfur suddenly begins to polymerize and the viscosity increases by more than two orders of magnitude over a range of 4°; but in this range the mobilities μ_- and μ_+ showed no significant change. The experimenters, in the belief that ionic mobilities (but not electronic) should vary inversely with viscosity, ascribed the mobilities in sulfur to electron hopping, but in N_2, CO and O_2 to ionic drift (presumably of impurity negative ions in N_2 and CO). However, Drickamer and coworkers [539005, 539006] showed that the rate of self–diffusion in liquid sulfur changes little over the range where viscosity increases, and the effect of pressure on self–diffusion showed the activation volume to be only 1 to 6 atomic volumes. Apparently diffusion of small molecules may occur with little hindrance within the network of polymer molecules, while viscous flow requires motion of the macromolecules. Ionic drift should be more closely related to self–diffusion than to viscosity, so it seems possible that in all these liquid elements the mechanism of charge transfer is ionic. However, this can hardly be true for the solid crystals, where electron hopping would seem to be the only plausible mechanism; and the fairly small change of mobility and its temperature coefficient on melting argues in favor of the same mechanism holding in both phases. The data on mobility of negative charge carriers in these liquids is therefore included in table 1, with the notation that interpretation of these numbers as electron mobilities is doubtful.

4.2. Hydrocarbons

Electron mobilities in hydrocarbons and tetramethylsilane (TMS) are shown in table 2. The aliphatic hydrocarbons, saturated and unsaturated, are listed first, in the order of carbon number, followed by the aromatic liquids.

TABLE 2. Zero–field mobility in liquid hydrocarbons

Name	μ_- cm^{2}V^{-1}s^{-1}	T, K	$E_{\text{activn.}}$ kcal/mole	Method[a]	Reference
Methane	400	111	Negative, small	tl	731036
	430	140	Negative, small	pc	741012
Ethane	0.8	200	See fig. 8	tl	739187 740317
	0.97	200	3	pc	741012
Ethylene	0.0030	170	—	pc	741012
Propane	0.55	238	3	pc	741012
	0.12	200	See fig. 8	tl	740346
Propylene	0.008	234	4	pc	741012
Cyclopropane	0.0043	234	4	pc	741012
n–Butane	0.073	250	4	pc	741012
	0.4	296	—	H	700140
Butene–1	0.064	293	—	pc	731035
cis–Butene–2	2.2	293	3.7	pc	731035
trans–Butene–2	0.029	293	5.4	pc	731035
Isobutane	5.	294	—	pc	720034
Isobutene	1.44	293	—	pc	731035

TABLE 2. Zero–field mobility in liquid hydrocarbons — Continued

Name	μ_- $cm^2V^{-1}s^{-1}$	T, K	$E_{activn.}$ kcal/mole	Method[a]	Reference
n–Pentane	0.16	296	—	H	700140
	0.08	300	—	ds	719062
	0.15	293	—	pc	731035
	0.14	296	—	H	741036
2–Methylbutene–2	3.6	300	2.6	ds	719062
Neopentane	68	296	0.32	ds	729022
	70	295	—	tl	739187
	70	258–296	0	pc	741111
Tetramethylsilane	90	296	—	H	700140
	100	223–292	0	H	750003
Cyclopentane	1.1	296	—	H	700140
n–Hexane	0.076	300	4.35	ds	729022
	0.09	296	5.5	H	700140
	0.082	296	—	H	741036
	0.069	294	—	H	750003
2,2–Dimethylbutane	10.	296	1.4	H	700140
	12.	295	—	tl	739187
2,3–Dimethylbutene–2	5.8	293	—	pc	731035
Cyclohexane	0.35	296	—	H	700140
	0.45	294	2.9	pc	720269
	0.24	296	—	H	741036
	0.22	294	—	H	750003
Cyclohexene	1.0	293	3.6	pc	731035
Methylcyclohexane	0.068	296	4.7	H	741036
2,2,4–Trimethylpentane	7.	296	—	H	700140
	5.3	293	1.16	H	750003
2,2,3,3–Tetramethylpentane	5.2	295	1.5	pc	720269
2,2,4,4–Tetramethylpentane	24.	295	1.4	pc	720269
2,2,5,5–Tetramethylhexane	12	293	1.1	pc	720269
Benzene	0.6	300	—	ds	719062
	0.11	293	7.4	pc	741110
Toluene	0.54	300	—	ds	729022
	0.063	293	3.4	pc	741110
o–Xylene	0.018	292	4.4	pc	741110
m–Xylene	0.057	292	4.5	pc	741110
p–Xylene	0.062	293	—	pc	741110
1,2,3–Trimethylbenzene	0.022	293	4.8	pc	741110
1,2,4–Trimethylbenzene	0.035	292	4.3	pc	741110
1,3,5–Trimethylbenzene	0.16	293	3.2	pc	741110
1,2,3,4–Tetramethylbenzene	0.040	323	5.	pc	741110

[a] Abbreviations: ds, double shutter; H, Hudson; pc, pulse conductivity; tl, thick layer.

The most striking feature of this work is the variation in the mobilities observed in the alkanes, which range over a factor of 1000 in a group of compounds whose other properties are very similar. There is a general correlation of mobility with other electronic properties — free–ion yields and V_0 values — but not with dielectric constants or other commonly listed properties. The most important factor in fixing μ_- seems to be the symmetry of the molecules. Those of nearly spherical shape — methane, neopentane, TMS — have the highest mobilities, and Bakale and Schmidt [731036, 739187] have shown that the apparent electron mobility in these compounds decreases with increasing field, as in liquid argon. The difference in electron mobilities between liquid ethane and methane is striking, and the field effects are actually opposite, with the apparent mobility at 200 K increasing in ethane at fields above 70 kV/cm [740317]. Propane behaves similarly to ethane, with the apparent mobility increasing above 100 kV/cm. In other hydrocarbons, the velocity remains proportional to the field up to the highest field studied. In all cases except methane and TMS, the observed mobilities as a function of temperature

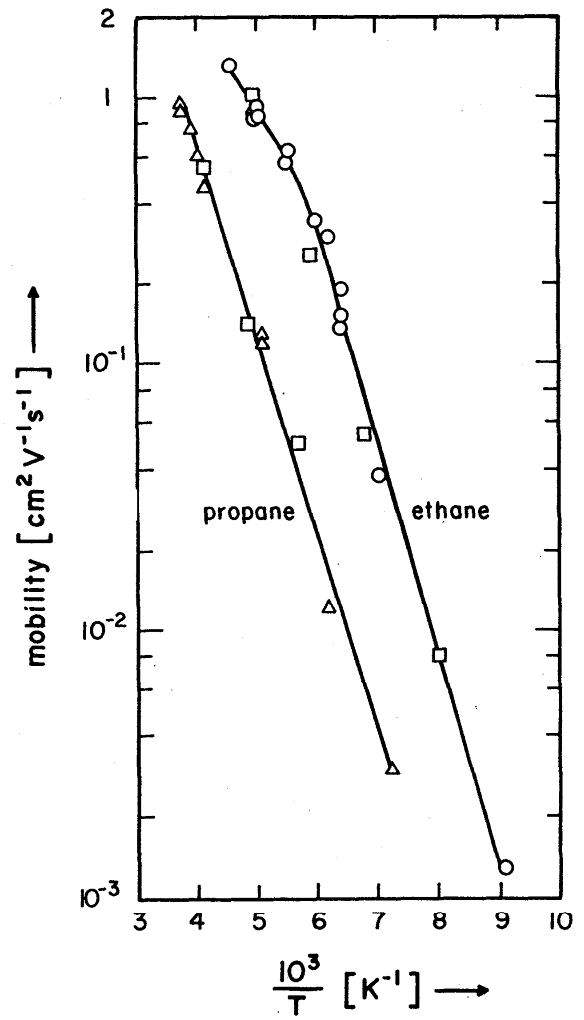

FIGURE 8. Temperature dependence of the electron low field mobility of ethane and propane. Ethane curve: circles, data from [740317]; squares, data from [741012]. Propane curve: triangles, data from [740346]; squares, data from [741012].

ppear to fit an Arrhenius expression, with the activation energies in general being lower the higher the room–temperature mobilities.

It is thought that molecular shape influences the mobility through the anisotropy of the polarizability in unsymmetrical molecules. Orientations of acyclic hydrocarbon molecules in a liquid are mainly random. If a group of neighboring molecules happens to have their directions of high polarizability oriented towards a central point, an electron coming to that point would be at a lower potential than at other points, and would tend to be localized there; the less symmetrical the polarizability, the deeper the traps. Electrons localized in such traps are solvated, and have the broad absorption spectrum in the infrared typical of solvated electrons in polar liquids (see, for example, [690400] and [710642]). It is reasonable to suppose that the only difference between the electrons in hydrocarbons and the permanently solvated, low conductivity electrons in polar solvents such as ammonia is that the traps in the latter are so much deeper that the equilibrium fraction of electrons in the conduction band is negligibly small. These qualitative considerations await confirmation by an actual calculation of the potentials in liquid hydrocarbons. Such a calculation, even for ethane, would be far more complex and difficult than for liquid argon.

The effect of the double bond in ethylene and propylene is to decrease the mobility by a large factor; but in larger molecules this effect is not seen. The remarkable difference in the electron mobility in the *cis* and *trans* forms of butene–2 emphasizes the dependence of this property on the molecular geometry.

Comparison of the results of different laboratories shows that the absolute accuracy is not always as good as the experimenters believed. The worst discrepancies appear with benzene and toluene; however, the experimenters who measured drift time reported that only 20% of the current appeared to be carried by the fast negative carriers, the rest being ascribed to impurity ions; the conductivity method would then be expected to give lower values. Somewhat discrepant values also appear for cyclohexane and normal pentane. In the case of neopentane, a number of lower reported values have been excluded from the table because they have been superseded by more recent values from the same laboratories.

4.3. Polar Solvents

Mobilities of solvated electrons in polar liquids are given in table 3. These measurements are all made by determining that part of the conductivity due to the electron, as outlined above. The results in water and ammonia are based on rigorous treatment of accurate data on conductivities and transference numbers, and should be good to a few percent; but the results on the other compounds are based on small deviations in conductivity decay curves brought about by small additions of anthracene or other electron acceptors, which are analyzed on the assumption that the mobilities of the acceptor negative ion and the positive ion are equal. The results are of interest chiefly in showing that the mobilities of solvated electrons in all these solvents are of comparable magnitude.

TABLE 3. Mobilities of solvated electrons in polar solvents

Solvent	μ_-	T, K	$E_{\text{activn.}}$ kcal/mole	References
Ammonia	0.0092	239	—	609010 for transference number; 599008 for conductance, recalcd. from 219001
Water	0.00197	298	—	690295
	0.00197	295	—	690547
	0.00187	298	4.8	700243
	0.00162	292	4.2	720404
Methyl ethyl ketone[a]	0.0015	293	—	720153
Hexamethylphosphoramide	0.00055	293	—	720153
Butylamine	0.0027	293	—	720153
Tributylamine	0.002	293	—	720153
Methyl alcohol	0.00059	293	—	710064
Ethyl alcohol	0.00025	293	—	710064
Isopropyl alcohol	0.00051	293	—	720574
Isobutyl alcohol	0.00068	293	—	720574
n–Butyl alcohol	0.00075	293	—	720153
	0.00073	293	—	720574
Isopentyl alcohol	0.00095	293	—	720153
	0.00097	293	—	720574
n–Hexyl alcohol	0.00043	293	—	720574
Ethylene glycol	0.00028	293	—	720574

[a] May be a molecular anion rather than a solvated electron.

5. Conduction Band Energies

Values of V_0 for various liquids at selected temperatures are shown in table 4. Temperature effects on V_0 are shown in figure 9 for those liquids for which values at more than one temperature were

TABLE 4. Conduction band energies V_0 in various liquids

Liquid	T, K	V_0, eV	References
Helium	4.2	+1.05	659054
Argon	84	−0.33	670195
	85	−0.18	750045
Xenon	163	−0.65	750045
Methane	109	0.0	740192
	95	0.0	749281
Ethane	182	+0.02	740192
Propane	222	−0.07	747297
n–Butane	271	+0.12	747297
cis–Butene–2	243	−0.16	750009
n–Pentane	295	+0.01	747297
	295	−0.01	720439
	295	+0.04	719091
	295	−0.02	750009
		−0.2	727460
Neopentane	295	−0.43	719091
	295	−0.35	720439
	295	−0.38	747297
Cyclopentane	295	−0.17	720439
	295	−0.21	747297
n–Hexane	295	+0.04	719091
	295	0.00	720439
	295	+0.1	747297
	295	+0.16	730414
	292	+0.02	750009
2–Methylpentane	295	+0.02	720439
	295	+0.01	747297
	295	−0.20	730414
3–Methylpentane	295	0.00	720439
	295	+0.01	747297
	295	−0.14	730414
2,3–Dimethylbutane	295	−0.10	730414
	295	−0.15	750009
2,2–Dimethylbutane	295	−0.15	730414
	295	−0.26	747297
2,3–Dimethylbutene–2	295	−0.25	727297
Cyclohexane	295	+0.01	727297
Methylcyclohexane	295	+0.08	727297
n–Octane	295	+0.13	727297
2,3,4–Trimethylpentane	295	−0.05	727297
2,2,4–Trimethylpentane	295	−0.18	719091
	295	−0.17	747297
2,2,5–Trimethylhexane	295	−0.10	747297
2,2,4,4–Tetramethylpentane	295	−0.33	747297
n–Decane	295	+0.18	747297
1,3–Dimethyladamantane	295	−0.30	747297
n–Tetradecane	295	+0.21	747297
Benzene	295	−0.14	730414
		−0.5	727460
Toluene	295	−0.22	730414
Tetramethylsilane	295	−0.62	719091
	295	−0.55	720439
	295	−0.59	747297
	293	−0.51	750009
Tetramethyltin	293	−0.70	750009

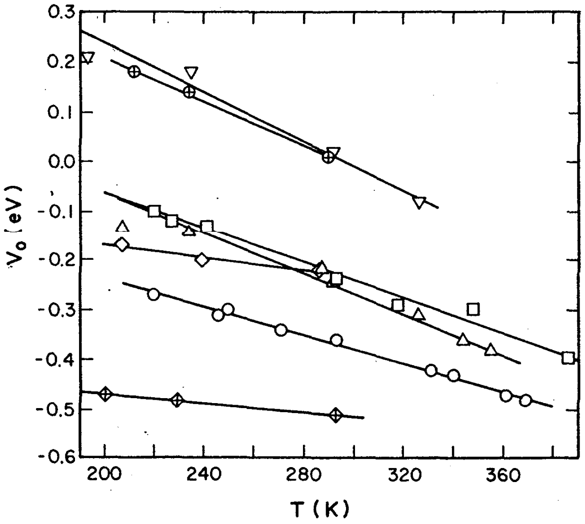

FIGURE 9. Temperature effects on V_0 values, from [750009]. Triangles (point down), *n*-hexane. Circles with cross, *n*-pentane. Squares, 2,2,5-trimethylhexane. Triangles (point up), 2,2,4-trimethylpentane. Diamonds, 2,2-dimethylbutane. Circles, 2,2,4,4-tetramethylpentane. Diamonds with cross, tetramethylsilane.

obtained by work function measurements. The method of photoionization of solutions gives only relative V_0 values for different solutes at any one temperature; the results for room temperature in [747297] and [727460] were assigned absolute numbers by comparing the results for a few liquids to the V_0 values previously determined for the same liquids by the work function method. Temperature effects on V_0 are not accurately determined by the photoionization method since the ionization efficiency at any wavelength may vary with temperature in an unknown manner. Consequently the V_0 values quoted in the above references for temperatures other than that of the room are not given here. Determinations by the work function method made on different days with different preparations reproduce to no better than ±0.05 eV. Determinations made on the same day reproduce to about ±0.02 eV.

Considerable effort has been expended on theoretical estimation of V_0. Lekner [670446] in the course of calculating the potential distribution in liquid argon for estimation of the mobility, obtained a value of −0.46 eV for V_0, compared with the experimental value of −0.33 eV. Springett, Jortner and Cohen [688042] developed a more general approximate expression, which in the case of argon gave a value of −0.63 eV. Miyakawa and Dexter [699050] provide an alternative approximate expression, which leads to similar results. Both methods use the gas–phase scattering length as a basic datum; and this may not be very accurately established experimentally. They also assume isotropic molecules, so the theories provide only a very rough guide for polyatomics. K. Fueki [728065] estimated by these methods V_0 for methane to be −0.74 eV, in poor agreement with later measured values 0.0; but he used an estimated value for the gas–phase scattering length; one hopes that use of an experimental value for this parameter would result in a better number for V_0. In these theories, V_0 is regarded as the sum of a negative polarization energy term and a positive kinetic energy term which results from the electron being restricted to the free volume. For liquid argon, these terms are respectively −2.50 and 1.87 eV, so that the sum, V_0, is the difference between two larger numbers and is accordingly inaccurate in absolute value.

The relation between V_0 and μ_e for aliphatic hydrocarbons has been much discussed. Comparison between the data of tables 2 and 4 shows a close correlation, especially for the linear and branched alkanes. N. R. Kestner and J. Jortner [738029] suggested an explanation in terms of a "percolation theory", in which V_0 is assumed to be linearly related to an "average electron energy" in the liquid, which in turn is related to the volume fraction of the liquid in which the electrons are in the quasifree condition. R. Schiller [730414] has developed a theory of the electron in a hydrocarbon based on the bubble model, assuming that the solvated state can be treated as an electron in a bubble of fluctuating size. The two theories lead to somewhat different relations between V_o and log μ_e. For a simple test of these theories, Holroyd and Tauchert [740079] measured V_o for a series of mixtures of *n*–hexane and neopentane, since it had been found (Minday *et al.*, [729022]) that log μ_e varied linearly with mole fraction in these mixtures. It was found that V_o was also linear with mole fraction, and hence with log μ_e, while the theories give a quite different prediction (fig. 7). A similar result was found in mixtures of hexane and tetramethylsilane. The linear relation found experimentally was unexpected, since many different factors have been thought to affect the values of V_o and μ_e. Further insights are needed.

Acknowledgements

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