Effect of Temperature on Conduction Band Energies of Electrons in Nonpolar Liquids[1]

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The energy of injection of an electron from vacuum into various nonpolar liquids was studied as a function of temperature. The method used was based on the difference in the photoelectric work function of zinc under vacuum and in the liquid; the difference: $\phi_{\text{liq}} - \phi_{\text{vac}}$, is denoted V_0. Measurements are reported for *n*-pentane, *n*-hexane, 2,2-dimethylbutane, 2,2,4-trimethylpentane, 2,2,5-trimethylhexane, 2,2,4,4-tetramethylpentane, and tetramethylsilane (Me_4Si). In all cases V_0 increases with decreasing temperature. The increase is largest for *n*-hexane (0.0024 eV/°C), less for the branched hydrocarbons (~0.0016 eV/°C), and smallest for Me_4Si (0.0005 eV/°C). The temperature dependence is roughly in accord with the Springett, Jortner, and Cohen model. The data on hydrocarbons show that V_0 increases as the free volume in the liquid decreases.

Introduction

Excess electrons in nonpolar liquids such as hydrocarbons occupy a band of states in which the electron wave function can be either localized or extended. The energy corresponding to the lowest extended state is referred to as the conduction band energy. Its energy relative to the energy of the electron under vacuum is denoted V_0, and the measurement of this quantity as a function of temperature is reported here. In the method used, V_0 is the difference in work function of a metal immersed in the liquid from its value in vacuo; thus $V_0 = \phi_{\text{liq}} - \phi_{\text{vac}}$. Most previous studies[2-7] utilized this method, but V_0 can also be determined by photoionization of solutes[8] as well as other methods.[9] All earlier photoelectric measurements were done at room temperature. However, the photoionization study[8] spanned a large temperature range and the results suggested that V_0 changes with temperature. Since the photoionization method is complicated by the temperature effect on both ion–electron separation probabilities and threshold behavior, this study utilizing the photoelectric method was undertaken to measure V_0 over a range of temperatures for several liquids.

The temperature dependence of V_0 is of interest because of the suggestion[10] that the rates of electron reactions in hydrocarbons are a function of V_0. It has also been observed that the equilibrium constant of electron attachment reactions is influenced by the energy of the conduction band,[11] and it was hoped that a temperature study would help evaluate the parameters involved.

Calculations utilizing the semicontinuum model indicate that V_0 should decrease with increasing temperature for alcohols.[12] A similar effect would be expected for other liquids since it is a consequence of changes in density with temperature. The model of Springett, Jortner, and Cohen[13] is used to calculate V_0 as a function of temperature for each liquid by normalizing to the value of V_0 at 20°.

Experimental Section

The photocell used in this study could be assembled and disassembled to permit resurfacing of the photocathode. A Varian flange with a copper gasket joined upper and lower parts of the cell. The lower part of the flange was sealed by Kovar to the outer quartz envelope of the photocell. The inner surface of the quartz, with the exception of the flat window, was coated with tin oxide. To the upper part of the flange was connected two stainless steel tubes (A) (see detail Figure 1), through which passed the high voltage and current leads. A valve was attached for connection to the vacuum line. The photocathode (C) was coated in a separate apparatus by slow evaporation of zinc from a tungsten filament. The zinc electrode was then transferred to the cell; this operation was done in a glove bag filled with N_2 to avoid exposure of the zinc to air. After assembly, the cell was washed with dry solvent and evacuated to 10^{-6} Torr. The light beam passed through an oval slot in the anode which was covered with mesh. The anode was maintained at a positive potential and the electrodes were separated by about 1 mm. For high-temperature work, the cell was placed in a temperature-regulated oven. Low temperatures were attained by cooling with a cold nitrogen gas stream.

Work functions were determined by the method outlined previously.[2] First the photoelectric response of the zinc surface as a function of wavelength was determined under vacuum at 20°C. Then the liquid was distilled into the cell and heated or cooled to the appropriate temperature and the response remeasured. After removal of the liquid, the vacuum response was repeated at 20°C.

The current (i) from a phototube is given by

$$i/T^2 = \alpha A F(x) \tag{1}$$

where F(x) is Fowler's function and x is $(h\nu - \phi)/kT$. The data were fit to this equation to determine the work function (ϕ). A set of data was not accepted unless the two vacuum work functions agreed to within 0.02 eV. Generally for clean zinc surfaces the data gave a reasonably good fit to the Fowler function in both the liquid and the vacuum (see Figures 2 and 3 in Results). Since this function applies only near the threshold, measurements that were more than 30 $h\nu/kT$ units above the work function were not used in the least-squares analysis. Typically a zinc surface could be used over a period of weeks without significant change in the work function.

Most liquids used in this study were first passed through activated silica gel, degassed, and stirred over NaK alloy. The only exception to this treatment was tetramethyltin (Alfa, electronic grade), which was dried over anhydrous

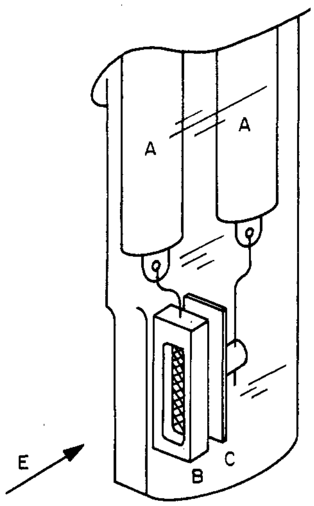

Figure 1. Detail of photocell: (A) stainless steel electrode supports, (B) anode (wire mesh over central hole is 80% transparent), (C) zinc-coated cathode, (D) quartz envelope coated on inside with SnO_2, (E) light beam (enters through flat quartz window).

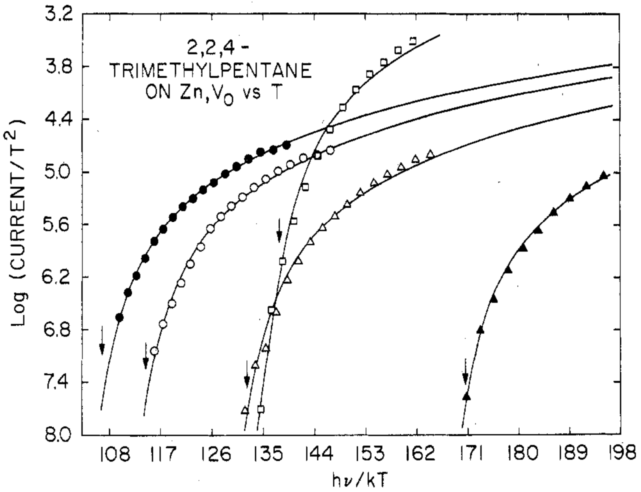

Figure 2. Spectral response of photocell, log (i/T^2) vs. $h\nu/kT$ at $E = 10^4$ V/cm: □ vacuum at 20°, ϕ = 3.54 eV. Filled with 2,2,4-trimethylpentane: ▲ at −39°, ϕ = 3.44 eV; △ at 18°, ϕ = 3.32 eV; ○ at 53°, ϕ = 3.23 eV; ● at 71°, ϕ = 3.19 eV.

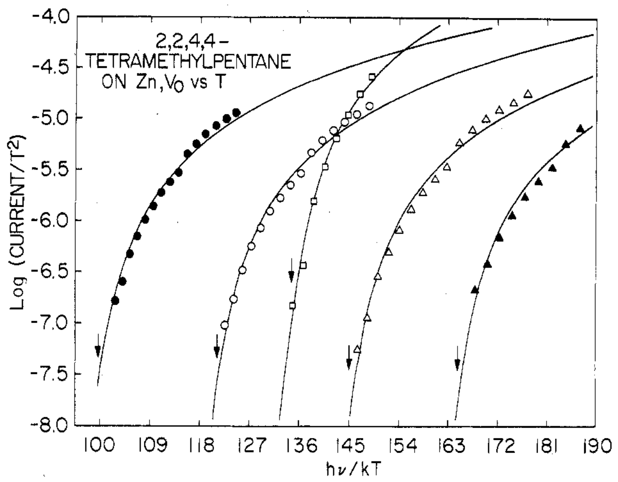

Figure 3. Spectral response of photocell, log (i/T^2) vs. $h\nu/kT$ at E = 5000 V/cm: □, vacuum at 20°, ϕ = 3.41 eV. Filled with 2,2,4,4-tetramethylpentane at: ▲, −53°, ϕ = 3.13 eV; △, −26°, ϕ = 3.09 eV; ○, 21°, ϕ = 3.06 eV; ●, +58°, ϕ = 3.01 eV.

$CaCl_2$ and degassed without NaK treatment. Most hydrocarbons were Phillips Research Grade; 2,2,4,4-tetramethylpentane was from Chemical Samples, 2,2,5-trimethylhexane was Phillips Pure Grade (99%), and 2,3-dimethylbutene-2 was from Aldrich. Densities were taken from published compilations where available or from extrapolations of the type given by Francis.[14]

Results

The work function of Zn immersed in several nonpolar liquids was measured as a function of temperature. Figures 2 and 3 show typical spectral data obtained for 2,2,4-trimethylpentane and 2,2,4,4-tetramethylpentane, respectively. These are plots of $\log(i/T^2)$, where i is the normalized photocurrent vs. the photon energy parameter $h\nu/kT$ (see eq 1). The solid lines are the Fowler curves computed by least squares to fit the set of data at each temperature. The fit of the data to the Fowler curves is as good for the liquid as for the vacuum. The work function is derived from the shift in the Fowler curve along the $h\nu/kT$ axis and corresponds to a specific value of $h\nu_0$ (indicated by the arrows in the figures). The figures show clearly that ϕ_{liq} decreases with increasing temperature for both liquids; the actual decrease for 2,2,4-trimethylpentane is −0.18 eV and for 2,2,4,4-tetramethylpentane is −0.14 eV over a 100° temperature range. (Note the use of the parameter $h\nu/kT$ in the figures tends to exaggerate this effect.)

In addition to the two liquids, for which results are given in Figures 2 and 3, detailed measurements of V_0 vs. temperature were also obtained for n-pentane, n-hexane, 2,2-dimethylbutane, 2,2,5-trimethylhexane, and tetramethylsilane (Me_4Si); the results are given in Table I. Also shown are some new work function measurements for *cis*-butene-2, 2,3-dimethylbutene-2, and tetramethyltin. For these liquids, V_0 was measured only at one temperature. For tetramethyltin at 20°, V_0 is −0.75 eV, which is the lowest value reported for any liquid and is attributed to the highly polarizable tin atom which enhances the polarization energy, thus lowering V_0 (see Discussion).

For the liquids studied, V_0 decreases with increasing temperature; this effect for four liquids is shown in Figure 4. The decrease is approximately linear with temperature up to the highest temperatures studied, around 100°C. The slope dV_0/dT is greatest for n-hexane (−0.0024 eV/deg), somewhat less for the branched octanes and nonanes (~−0.0016 eV/deg), and even less for Me_4Si (−0.0005 eV/deg). A V_0 value less than −0.5 eV has not yet been observed for a hydrocarbon. Comparison of the present results with the earlier photoionization results[8] indicates good agreement for n-hexane, but a much smaller slope for Me_4Si.

From the data in Figure 4, it may be noted that V_0 for n-hexane at +80° is approximately the same as V_0 for 2,2,4-trimethylpentane at −80°. Similarly, V_0 for 2,2,4-trimethylpentane at +70° is comparable to V_0 for neopentane and 2,2,4,4-tetramethylpentane at 20°. Comparable values of V_0 indicate the liquids may correspond in some other property (see Discussion). It is also interesting to note that molecules with similar molecular structure have very similar values of V_0 and similar temperature effects: thus at room temperature neopentane and 2,2,4,4-tetramethylpentane have the same V_0; at all temperatures the V_0 values for 2,2,4-trimethylpentane and 2,2,5-trimethylhexane are similar as are those for n-pentane and n-hexane.

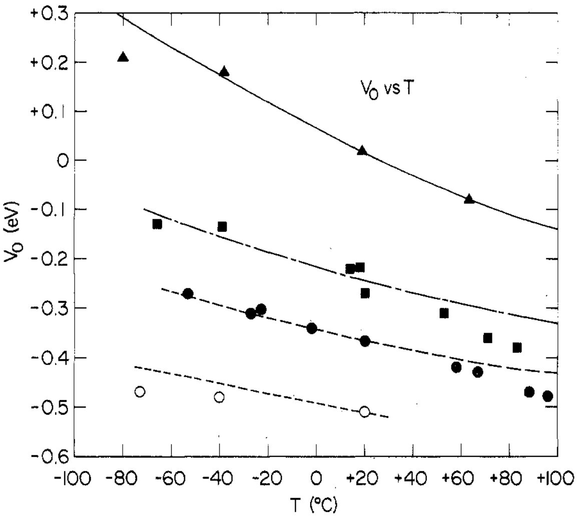

Figure 4. Plot of V_0 vs. temperature. Points are experimental; lines are calculated from Wigner–Seitz method: *n*-hexane (▲, —), 2,2,4-trimethylpentane (■, — - —); 2,2,4,4-tetramethylpentane (●, — — —); tetramethylsilane (○, - - - -).

Results presented here indicate that the magnitude of the photocurrent observed from liquid-filled photocells is not very temperature sensitive. Figures 2 and 3 show that as the temperature increases there is little or no shift in the Fowler curve along the y axis. The current depends on two main factors: the yield of electrons from the photoelectric effect, which varies as T^2 (see eq 1), and the probability of escape from the image potential. The data in Figures 2 and 3 have been plotted as log (i/T^2); thus any vertical shifts in the Fowler curves with temperature must be attributed to changes in the escape probability. This probability is a function of the field, the range of the injected electrons, and the temperature. The theory for this in the one-dimensional Onsager case has been worked out in detail.[3,15,16] The effect of temperature in the diffusion theory has been examined specifically by Blossey.[16] Our results appear to be in reasonable accord with this theory. In most instances the theory predicts the current will decrease with increasing temperature, although if the range is small there will be an increase. For the conditions applicable to Figures 2 and 3, a small decrease (14%) over a 110° temperature rise is predicted, which is in reasonable accord with experiment.

Discussion

Temperature Dependence of V_0. The data in Figures 2–4 and in Table I show that V_0 decreases with increasing temperature. This means that the V_0 level decreases as the free volume in the liquid increases. Since the Springett, Jortner, and Cohen model[13,17] for calculating V_0 predicts a change in this direction, it is of interest to compare the results with those of the model. The method was originally developed for rare gas liquids but has been applied to hydrocarbons[18-20] to calculate the hard core radius a from experimental V_0's (a defines the sphere from which the electron is excluded in the model). Here we use values of V_0 measured at 20° to calculate a from which V_0 is calculated at other temperatures. The conduction band energy is given by

$$V_0 = T_0 + U_p \tag{2}$$

where U_p is the long-range polarization energy assumed to be a constant given by

TABLE I: V_0 vs. Temperature

Liquid	Temp, °C	V_0 Exptl	V_0 Calcd[a]	a
n-Pentane	−61	+0.18	+0.21	
	−39	+0.12	+0.17	
	+17	+0.01	(+0.01)	2.03
n-Hexane	−80	+0.21	+0.29	
	−38	+0.18	+0.17	
	+19	+0.02	(+0.02)	2.17
	+63	−0.08	−0.08	
2,2-Dimethylbutane	−66	−0.17	−0.08	
	−34	−0.20	−0.14	
	+13	−0.22	(−0.22)	2.11
2,2,4-Trimethylpentane	−66	−0.13	−0.11	
	−39	−0.14	−0.16	
	+14	−0.22	−0.24	
	+19	−0.24	(−0.24)	2.34
	+53	−0.31	−0.28	
	+71	−0.36	−0.30	
	+83	−0.38	−0.31	
2,2,5-Trimethylhexane	−53	−0.10	−0.12	
	−46	−0.12	−0.14	
	−32	−0.13	−0.16	
	20	−0.24	(−0.24)	2.45
	45	−0.29	−0.27	
	75	−0.30	−0.31	
	+113	−0.39	−0.34	
2,2,4,4-Tetramethylpentane	−53	−0.27	−0.27	
	−27	−0.31	−0.31	
	−23	−0.30	−0.31	
	−2	−0.34	−0.34	
	20	−0.36	(−0.36)	2.40
	58	−0.42	−0.40	
	67	−0.43	−0.41	
	88	−0.47	−0.42	
	96	−0.48	−0.43	
2,3-Dimethylbutene-2	+13	−0.15	(−0.15)	
cis-Butene-2	−30	−0.16		
Tetramethyltin	20	−0.75		
Tetramethylsilane	+20	−0.51	(−0.51)	2.02
	−40	−0.48	−0.45	
	−73	−0.47	−0.42	

[a] V_0 was calculated for temperatures other than 20° by using the method in ref 12, in which the a value is derived from the value of V_0 at room temperature. Assumed V_0's in parentheses.

$$U_p = \frac{-3\alpha e^2}{2r_s^4}\left[\frac{8}{7} + \left(1 + \frac{8\pi\alpha n}{3}\right)^{-1}\right] \tag{3}$$

α is the molecular polarizability and T_0 is the zero-point kinetic energy given by

$$T_0 = \hbar^2 k_0^2/2m \tag{4}$$

The Wigner–Seitz radius r_s is related to the number density n by $\frac{4}{3}\pi r_s^3 = n^{-1}$ and k_0 is determined by

$$\tan k_0(r_s - a) = k_0 r_s \tag{5}$$

From these equations one expects that T_0 will decrease with decreasing density, that is, as r_s increases. However, from eq 3, U_p also increases as r_s increases and any change in V_0 will be determined by the relative changes in these two energy terms. For these hydrocarbons the calculated change in the T_0 term is greater than the change in the U_p term, and a decrease in V_0 with increasing temperature is expected. The calculated values are shown in the last column of Table I and as the lines in Figure 4. Overall the agreement with experiment is remarkably good, especially for n-hexane. Also a smaller change with temperature is

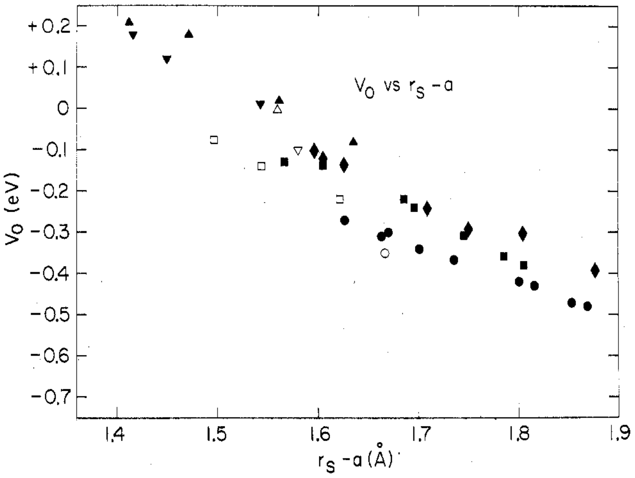

Figure 5. Data on V_0 at different temperatures plotted vs. $r_s - a$. This work: ▲, *n*-hexane; ▼, *n*-pentane; ■, 2,2,4-trimethylpentane; ●, 2,2,4,4-tetramethylpentane; ◆, 2,2,5-trimethylhexane; □, neohexane; ○, neopentane (ref 6, 8); △, 3-methylpentane and 2-methylpentane (ref 3); ▽, 2,3-dimethylbutane (ref 7).

predicted for Me_4Si and 2,2,4,4-tetramethylpentane than for *n*-hexane, as is observed experimentally. Thus it seems justifiable, based on this and other evidence,[20] to employ the Springett–Jortner–Cohen model as we have done. The calculation indicates the change (dV_0/dT) becomes less above 100°.

In order to ascertain the nature of the free volume dependence of V_0 and to show the importance of this parameter, we plotted the data as a function of $r_s - a$ in Figure 5. Figure 5 includes all the data for saturated hydrocarbons reported here and from previous work function data. The points tend to follow a single curve, V_0 decreasing monotonically as the distance $r_s - a$ increases. The points for the more symmetrical molecules like neopentane and 2,2,4,4-tetramethylpentane lie somewhat below the rest. In contrast, in plots of V_0 vs. temperature (as in Figure 4) or vs. density the points for each liquid lie on completely separate curves. The points for Me_4Si and TMT (not shown) lie significantly below the line; which indicates that the presence of a polarizable atom has an added effect on V_0. The correlation with $r_s - a$ thus applies only to hydrocarbons. The assumption of an isotropic value of a derivable from V_0 may not be valid in all cases. It appears to apply here perhaps since most of the molecules studied are not too unspherical. Since molecular volumes can be estimated from V_{crit}, it has been suggested[20] that the electron molecule hard core radius a can likewise be estimated from V_{crit}. From examination of all the available data the relationship $a = 0.303V_{crit}^{1/3}$ has been suggested[21] (a is in Å and V_{crit} is in cm^3/mol). If a is estimated in this way and the data plotted as in Figure 5 the same general trend is obtained. The figure does provide a rationale why V_0 is the same for *n*-hexane near +80° and 2,2,4-trimethylpentane near −80°: because the two liquids have corresponding values of the $r_s - a$ parameter (1.6 Å) at these conditions. The dependence on $r_s - a$ also suggests that high pressures should lead to an increase in V_0. We conclude from these results that in nonpolar liquids there are regions of molecular size from which the electron is at least partly excluded.

It has been known since the early work of DuBridge and others[22,23] that the temperature effect on the vacuum work function is small (~10^{-4} V/deg). However, here we find for injection into a liquid that temperature changes the work function and, consequently, V_0, and the effect is an order of magnitude greater than in vacuo. From the results, this effect can be expressed by

$$V_0(T) = V_0^0 + \alpha T \qquad (6)$$

where α has values from −0.0005 to −0.0024 eV/deg depending on the liquid.

References and Notes

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Discussion

M. H. COHEN. The reported correlation of V_0 with $r_s - a$ and therefore free volume suggests a very amusing correlation of V_0 with viscosity and the glass transition which also correlates with free volume. It should also be pointed out that the presence of the liquid outside the metal will reduce the image potential experienced by the electron and affect the injection current thereby.

R. HOLROYD. The correlation with $r_s - a$ is independent of the model we chose.

J. JORTNER. (1) The definite experiment for the determination of V_0 will be the measurement of the threshold, E_I, for internal photoionization of an impurity, as you have done, together with the threshold, E_E, for external photoionization whereupon $V_0 = E_I - E_E$. The only difficulty involves the corrections for the escape length, L, of electrons in the liquid in the determination of E_E. We have conducted such experiments in doped solid rare gases, where L is large (~1000 Å). The latter case is much simpler, while in polar liquids where L is relatively small appropriate corrections have to be introduced.

(2) The model of Springett, Jortner, and Cohen (SJC) for V_0 in nonpolar fluids was advanced for the quasi-free electron state. Without dwelling on technical details, I would like to point out that for liquid hydrocarbons where the electron mobility is low the electron is not quasi-free. Kestner and I attempted to treat this problem in terms of an inhomogeneous percolation picture. In this case the SJC model is inapplicable.

B. WEBSTER. Could I just follow up the earlier remark of J. Jortner. In $[Fe(CN)_6]^{4-}$ an electron ejection into the liquid has an onset at >3.82 eV. Direct emission into the vapor occurs at >5.25 eV. Is the difference really a measure of $V_0 \sim -1.33$ eV or should this be regarded as the electron affinity of water?

J. Jortner. I am well familiar with the photoemission work from ferrocyanide solutions conducted by Delahay and his colleagues. I wonder whether the experimental value for internal photoionization in this system is reliable. Photochemical evidence can be misleading as excited states such as that of ferrocyanide in solution can yield an electron by thermal ionization.

L. Kevan. (1) Question: Do V_0 values for methane and ethane fit on the correlation plot of V_0 vs. free volume?

(2) Comment: You pointed out that the temperature dependence of V_0 for alkanes depends theoretically on the balance between the temperature dependence of the two component terms of V_0 ($V_0 = T_0 + U_p$), where T_0 is the kinetic energy and U_p is the polarization energy. In alkanes, including methane in which the electron is in a quasi-free state like in argon, T_0 decreases more than U_p increases with increasing temperature so V_0 becomes more negative. However, in argon the increase in U_p with temperature is almost exactly compensated for by the decrease in T_0 with temperature, so that V_0 is predicted to be essentially temperature independent. Thus the expected temperature dependence of V_0 depends on the medium.

R. Holroyd. Ethane is on the line. However, methane is somewhat below the line, especially if we use Tauchert and Schmidt's more recent value of $V_0 = -0.2$ eV. But the symmetrical molecules (like neopentane) are all on the low side. It is interesting that argon and methane have the same values for the $r_s - a$ parameter and comparable V_0's, which fits in with our correlation.

M. Silver. Using the Fowler plot to determine V_0 is very questionable because the Fowler method presumes that the limitation on the current is solely due to the flux of electrons from the electrode capable of entering the medium. However, experimentally one observes a field dependence of current implying that scattering in the medium and the specific potential distribution near the electrode are important. Unless the momentum exchange scattering and the energy loss (inelastic) scattering have the same energy dependence, there will be reflections back into the electrode which vary with $h\nu$. Since one measures a current, the $h\nu$ dependence of the current will reflect the energy dependence of the scattering events as well as the flux of electrons (Fowler emission). A simple calculation involving inelastic scattering and involving the excitation of vibrations could give an *apparent* positive energy shift of V_0 by the vibrational energy of approximately 0.1 or 0.2 eV. This calculation is equivalent to the one-dimensional Onsager escape probability over an arbitrary shaped barrier but including scattering of the hot electrons as well as diffusion of the thermalized electrons. . . . The correct procedure to use to obtain V_0 from photoinjection experiments is a careful study of the current–voltage characteristics at each $h\nu$ to obtain the scattering parameters and, of course, to use the Fowler plot on the current corrected for back scattering.

R. Holroyd. We use the Fowler function to fit the data in the liquid because empirically the spectral dependence is the same as in vacuo. The current–voltage dependence is nearly ohmic, independent of wavelength, and this dependence is entirely accounted for by diffusion from the image charge under the applied field (see ref 3), and does not in itself imply back scattering. If the fraction of electrons back scattered is independent of wavelength, the Fowler function should apply. Any errors due to this problem are, I believe, minor and the photoelectric effect is at present the best method available to measure V_0

P. Delahay. Two comments: (1) A treatment of photoelectron emission into dielectrics is available (Brodskii). If I recall his theory (about 1970), the threshold extrapolation depends on the dielectric constant, e.g., with the power 5/2 of photon energy at high dielectric constants. It can be very different from the Fowler theory. (2) V_0 is a bulk property. Your definition of V_0 involves also the difference between the surface potentials of the metal in vacuo and the surface potential on the metal in the liquid. This term may not be entirely negligible. Moreover, the dipole induced in the electric field at this interface would orient at the interface orientation should be temperature dependent.

R. Holroyd. The 5/2 power applies only for $\epsilon > 10$; for $\epsilon \sim 2$, the Brodskii treatment shows the Fowler equation is applicable.

G. R. Freeman. (1) Although measurements in the 1930's showed little temperature dependence of the work functions of metals, did you check the temperature dependence with your apparatus?

R. Holroyd. Yes, and we find in agreement with DuBridge et al. little change in ϕ_{vac} with temperature.

G. R. Freeman. (2) Calculations with several recent models that correlate V_0 with electron mobilities in hydrocarbons indicate that ($V_0 - \bar{V}$), that is, the difference between the energies of the bound and quasi-free states, is nearly independent of temperature. Would you comment upon why $\bar{V}$ and V_0 should have similar temperature dependences?

R. Holroyd. I think others here are more qualified than I to comment on this. However, let me suggest that V_0 and $\bar{V}$ change together because the same factors, such as free volume, influence both states.