Field Emission and Field Ionization in Condensed Phases

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Field emission consists of electron tunneling from a conductor under the influence of a high applied electric field, which deforms the potential barrier at its surface (Figure 1). Usually the medium into which tunneling occurs is a vacuum; it is quite feasible, however, to obtain tunneling into normally insulating liquids or through liquid-like films adsorbed on the emitter. Such experiments can yield information on the heat of solution of electrons in condensed phases. Field ionization consists of field emission *from* atoms or molecules, *i.e.*, tunneling of electrons from these species under the influence of high fields. Again the process, normally carried out in a low-pressure gas, can occur in liquids and films. It can then yield information on the energy of filled levels, *i.e.*, the valence bands of such media.

Field emission and field ionization in liquids also provide controlled high-intensity sources of electrons and positive ions in liquids and readily yield the mobilities of the charge carriers. In addition, both reveal a number of high-field phenomena difficult or impossible to see by other means. By providing accurately known high fields and extremely well-characterized electrodes, they also shed light on breakdown phenomena in liquids. With the exception of field emission through Ne, Ar, Kr, and Xe layers[1] the subject matter of this paper is based mainly on recent work of Halpern and the author.[2,3]

We start with a very brief review of basic theory.[4] For present purposes it suffices to consider a metal as a potential well; because of the exclusion principle, only two electrons can occupy each translational level, so that the well will be filled to a depth of several electron volts, as shown in Figure 1. The highest filled level (Fermi level) is still several electron volts below the vacuum; this energy barrier is called the work function, ϕ. In thermionic emission electrons must be excited over this barrier; in field emission the application of a strong electric field deforms it, as shown in Figure 1b, so that electrons can tunnel *through* the resultant potential hill. The tunneling probability D is given with

reasonable accuracy by the WKB approximation

$$D \sim \exp\left(- 2\int_0^l k'\,dx\right) \qquad (1)$$

where

$$k' = (2m_e/\hbar^2)^{1/2}(V - E)^{1/2} \qquad (2)$$

and the integral extends from one end of the barrier to the other.

In a metal most of the emission comes from the vicinity of the Fermi level for which the barrier height is the work function ϕ; it is not hard to show that the dominant term in the Fowler–Nordheim equation[4] which relates current and field is

$$i \propto \exp[-(4/3)(2m/\hbar^2)^{1/2}\phi^{3/2}/F] =$$
$$\exp[-0.68\phi^{3/2}/F] \quad (3)$$

for ϕ in electron volts and F in volts per ångström, since the integral in (1) corresponds to a roughly triangular area of base ϕ/F and height $\phi^{1/2}$. For $\phi = 4.5$–5.5 eV fields of 0.3–0.6 v/Å are required for appreciable emission. The simplest way of obtaining these consists of etching a fine wire to a sharp point and surrounding it by a suitable anode, usually hemispherical, with a radius of 1–10 cm. The field at a hemispherical tip of radius r_t at a potential V with respect to the outer electrode is roughly

$$F_t \sim V/5r_t \qquad (4)$$

for a smooth surface (obtained by heating the etched tip to high temperature under vacuum). Since tip radii of ≥ 500 Å are easily obtained, a few kilovolts suffice to give the required fields. Because of its small size the emitter is usually monocrystalline, with different orientations exposed. If the average work function, *i.e.*, that of the highly emitting regions, is known, the field-voltage proportionality constant can be determined from eq 3 and subsequently used to determine work function changes. If the anode consists of a fluorescent screen the device just sketched is a field emission microscope, invented by Müller[4] in 1937; its mag-

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(1) R. Gomer, *Aust. J. Phys.*, 13, 391 (1960).
(2) B. Halpern and R. Gomer, *J. Chem. Phys.*, 51, 1031 (1969).
(3) B. Halpern and R. Gomer, *ibid.*, 51, 1048 (1969).
(4) R. Gomer, "Field Emission and Field Ionization," Harvard University Press, Cambridge, Mass., 1961; R. H. Good and E. W. Müller, *Handb. Phys.*, 21, 293 (1956).
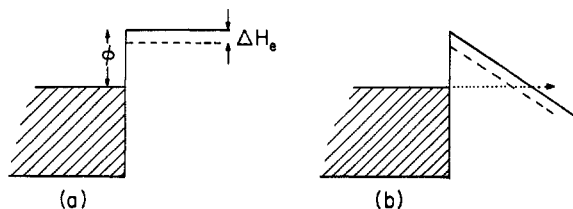
Figure 1. Schematic potential-energy diagram of a metal (a) in the absence and (b) in the presence of a negative field. Solid lines indicate a vacuum situation; dashed lines indicate the presence of a medium with electronic heat of solution $-\Delta H_e$.

nification stems from the fact that the electron trajectories follow the lines of force, which diverge almost radially from the emitter.

If the potentials in a field-emission microscope are reversed and a small pressure of gas is introduced, field ionization of the latter can occur at $F = 2\text{--}4$ V/Å, depending on the ionization potential of the gas. The process is essentially tunneling of electrons from a gas atom or molecule, under the influence of the high field (Figure 2). The rate of tunneling, τ_t^{-1}, can be calculated, somewhat primitively, by combining eq 1 with an electronic frequency, ν_e, of, e.g., 10^{15} sec^{-1}. One form of the result,[3] near a metal surface, is

$$\tau_t^{-1} = \nu_e \exp[-0.68(I^{3/2}g - \phi^{3/2})/F] \qquad (5)$$

where I is the ionization potential and $g(F^{1/2}/I)$ is a correction term analogous to an image correction in field emission.[4] Since electrons can tunnel only into empty metal states, ionization can occur only if

$$Fex \geq (I - \phi) - e^2/4x \qquad (6)$$

where the last term is an image potential contribution. Since the latter is usually small, eq 6 gives a critical ionization distance, x_c, which turns out to be 5–10 Å under

$$x_c \cong (I - \phi)/Fe \qquad (7)$$

most conditions.

A more quantitative approach is provided by perturbation theory; for present purposes WKB theory suffices. For completeness it should be mentioned that field ionization is the basis of the field ion microscope invented by Müller in 1950.

Field Emission in Liquids

A convenient method consists of filling a suitably modified field-emission microscope (Figure 3) with the liquid under study after first determining the field-voltage relation under ultrahigh vacuum. Since the potential distribution is unchanged if the entire tube is filled with liquid, this relation is preserved. In many cases it is possible, by cryogenic or gettering techniques, to purify the liquid sufficiently to prevent adsorption of impurities on the emitter when immersed in liquid so that meaningful work function measurements can be made. It is also possible to restore vacuum conditions and thus to examine the emitter for changes by running the device as a field emission microscope. In the experiments to be described the emitter material was tungsten,
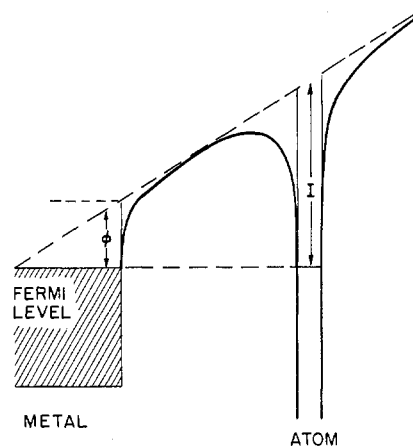

Figure 2. Diagram illustrating field ionization from an atom or molecule near a metal surface. ϕ, work function of metal; I, ionization potential of atom.
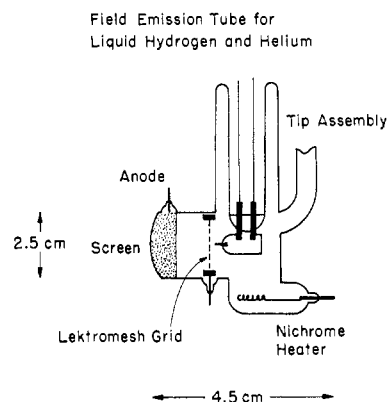

Figure 3. Schematic diagram of a field-emission tube for liquids.

chosen for its toughness and ease of fabrication. A rather wide range of phenomena is encountered in various systems; the following examples will illustrate these.

The current–voltage curve obtained with liquid H_2 (or D_2) is shown in Figure 4. The low-current regime fits the Fowler–Nordheim equation, while at high currents $i^{1/2} \propto V$; it will be shown later that this corresponds to a space-charge regime. Very different behavior is encountered with He, both above and below the λ point. At 4.2°K emission sets in abruptly at 0.23 V/Å with $i \geq 10^{-9}$ A (which is several orders of magnitude above the current estimated from eq 3). When the voltage is reduced below the onset value, emission continues and finally cuts off sharply at much lower voltage. After this initial surge there is almost no hysteresis, and the curve can be retraced. Examination of the emitter under vacuum shows considerable sputtering damage and local field enhancement by microscopic protuberances, although no appreciable change in r_t occurs. The details of the i–V regime are complicated, but at sufficiently high currents a "normal" space-charge regime occurs. Below the λ point currents, for given V, are larger by an order of magnitude. In the case of O_2 *only* a space-charge regime, as well as severe emitter blunting, is observed. With Ar,
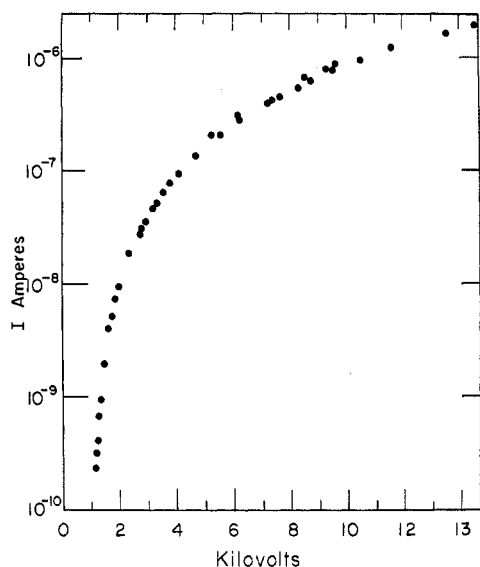
Figure 4. Plot of ln i vs. voltage for field emission into liquid H_2 at 21°K.

emission sets in abruptly with $i \sim 10^{-7}$ A at $F \sim 0.12$ V/Å (where emission under vacuum would be many orders of magnitude less), and there is severe emitter damage; a pinpoint of purple light can be seen at the tip. Unlike all the other cases examined, Ar does not give a $i^{1/2} \propto V$ space-charge regime unless contaminated with oxygen. For pure Ar $i \propto V$ both in direct current and microsecond pulsed emission even at the highest currents.

Several generalizations can be made at once: a true field-emission (Fowler–Nordheim) regime can be observed only if electron mobilities are high enough to prevent appreciable space charge (at least at low currents) and if energy-losing collisions are efficient enough to prevent electrons in the high-field region at the emitter from acquiring enough energy to ionize atoms or molecules of the liquid. In H_2, at 0.3 V/Å, the acceleration length for ionization is $\sim$50 Å, but charge multiplication does not occur; for He at 0.23 V/Å it is almost 100 Å, but avalanching does take place, as also in Ar, indicating that electron energy can be dissipated efficiently only by vibrational and/or rotational degrees of freedom. Emitter damage at high currents indicates that the considerable local heating near the tip leads to gas bubble formation and thus to a gaseous discharge, in which ion bombardment of the emitter occurs. It is not difficult to show[2] that a maximum temperature rise of

$$T_{\max} = F_t i / 32 \pi \kappa \qquad (8)$$

occurs at $r = 2r_t$ for concentric sphere geometry, κ being the thermal conductivity. For real systems a somewhat smaller rise must occur, but it can be shown that bubble formation should occur approximately at the currents where emitter damage is in fact observed.

Thus the mechanism of very high current generation in He and Ar must consist of charge multiplication in the liquid, rapidly followed by bubble formation and a local gaseous discharge. In the case of He the results with conditioned emitters indicate that it is also possible

to maintain charge multiplication regimes in the liquid, without bubble formation at moderate currents. Apparently this happens because local field enhancement for conditioned emitters permits emission at voltages sufficiently low to avoid heating to the point of bubble formation. The details of the "liquid-discharge" regime seem quite complex and are not well understood.

The results for O_2 indicate that field emission may be complicated by electrochemical effects. To date, no attempt has been made to investigate in any detail high-field phenomena of this sort in nonpolar media.

Although avalanching and space charge effects can mask the field-emission regime proper, the latter is observable in H_2, and of considerable theoretical interest. As a first approximation it probably suffices to take account of the medium by replacing the vacuum level by the average potential energy of electrons in the medium, i.e., shifting it by $-\Delta H_e$, the electronic heat of solution; it is convenient to think of this as defining the bottom of a conduction band. The ϕ in eq 3 is thus modified, and now corresponds to the energy difference between the Fermi level and the bottom of this band. The results for liquid H_2 indicate that the bottom of the band lies above the vacuum level by 0 to 0.5 eV. The uncertainty in this result comes from the fact that slight changes on the emitter are noted after emission into the liquid, even for very low current levels, which reduce the effective vacuum work function. It is not yet completely clear to what extent these changes should be counted in computing the work function change in liquid. It should be possible to resolve this point by using a variety of emitter materials of varying work function. It is in accord with recent theoretical predictions[5] that a free electron should have a negative heat of solution in liquid H_2, because the strong repulsion between the extra electron and the closed shell of H_2, resulting from the orthogonality requirement, is not sufficiently compensated by polarization. The lowest energy state of an electron in liquid H_2 is probably a bubble, as it is in He; the present results refer to a *free* electron, since the effective mass of an electron in a hole would be so high as to make tunneling prohibitively slow.

Field Emission through Films

Since avalanching makes it impossible in many cases of interest to measure work function changes in bulk liquids, field emission through physisorbed multilayers, thick enough to "cover" the tunneling barrier, offer an interesting alternative,[1] although it is not always clear whether these are more liquid-like or solid-like. Since 99.9% of the emission comes from within 1 eV of the Fermi level, the effective barrier length $\le$ 30 Å under most conditions so that four–five atomic layers suffice to cover it; since electron kinetic energy is negative in the barrier region, avalanching cannot occur. Film experiments can be carried out by more or less conventional field-emission microscopy at sufficiently low tem-

(5) B. E. Springett, J. Jortner, and M. H. Cohen, *J. Chem. Phys.*, **48**, 2720 (1968).

perature. For gases like Ne, Ar, Kr, or Xe, it is possible to work under ultrahigh vacuum by immersing the entire apparatus in liquid H_2 or He and to deposit the adsorbate on the emitter by sublimation or other techniques. It is also possible to study H_2 films[6] at $\leq 4.2°K$ by working at the vapor pressure, $\sim 2 \times 10^{-7}$ Torr.

Film experiments also reveal interesting facts about physical adsorption, although in the present context only the barest outline can be given. First, it turns out that considerable work function changes accompany formation of the first layer[1,7,8] for Ar, Kr, and Xe, with electron transfer *from* the adsorbate; the resultant dipoles lead to considerable ad–ad repulsion. For higher layers appreciable dipole moments are absent, and there is attractive interaction. This causes layers to evaporate preferentially from their edges; since the highest layer evaporates most rapidly, concentric rings are developed in the emission pattern and make it possible to count the number of layers. In the case of Ne, where the dipole moment is very small, cohesion is observed even in the first layer.[1]

The heat of physisorption of H_2 on tungsten (covered by a chemisorbed H layer) is so small that field-emission currents can cause desorption. Unlike the case where the entire tube is filled with dielectric, the field in a thin shell is reduced by $1/K$, K being a dielectric constant, so that for layers thinner than the barrier width emission depends on film thickness. In addition, back scattering and matching of the wave function at the layer edge may also make emission sensitive to thickness for slightly thicker layers. This, combined with the heating, leads to current hysteresis and bistable $i–V$ regimes: for thick layers (low branch) desorption starts once the current reaches a certain value; the current then rises almost instantaneously, to a point where all but the first one or two molecular layers are gone. If V is decreased, i follows the high branch until suddenly thickening and switching to the low branch occur.

With He on clean tungsten[6] the heat of adsorption seems too small to permit even monolayer formation at $4.2°K$ and 10^{-5} Torr (the maximum pressure allowable for field emission); even at $1.6°K$ not many layers seem to form. Interestingly enough the presence of oxygen on the emitter seems to increase the adsorption energy sufficiently to permit multilayer formation at $\sim 2°K$, as indicated by current hysteresis. The effect of oxygen for He adsorption is thus opposite to that of the higher inert gases where it leads to decreased adsorption energies and dipole moments.[7]

If dipole moments in the first layer are unaffected by further adsorption, $-\Delta H_e$ is given by the difference between the monolayer and multilayer work functions; the former must be determined when multilayers are absent, which is generally easy, since there is an appreciable difference in binding energy between the first and higher layers. Recent single plane measurements for mono- and multilayer adsorption of Kr on W[8] show that

Table I
Enthalpies of Solution of Electrons in Some Liquids

Substance	ΔH_e (free electron), eV	ΔH_e (other), eV
H_2	≥ 1.2	
Ne	-0.8 to -0.74	
Ar	-0.6 to -0.45	-0.45 ± 0.2;[a] 0.33[b]
Kr	-1.4 to -1.0	-0.75 ± 0.2[a]
Xe	-1.4 to -1.3	

[a] Spectroscopic, Xe in liquid Ar or Kr: B. Raz and J. Jortner, *Proc. Roy. Soc., Ser. A*, **317**, 113 (1970). [b] Photoelectric: B. Halpern, J. Lekner, S. A. Rice, and R. Gomer, *Phys. Rev.*, **156**, 351 (1967).

the difference between these is almost independent of crystal plane, although the ϕ values themselves vary widely. In addition, the difference is close to that previously determined from average ϕ measurements. This suggests that the first layer is not appreciably affected by subsequent adsorption. Since the field in the layer is reduced by $1/K$ the vacuum field–voltage proportionality constant must be reduced by this amount, or equivalently the apparent ϕ value for multilayers obtained from it and eq 3 must be divided by $K^{2/3}$. Thus

$$\Delta H_e = -\Delta\phi = \phi_{mono} - \phi_{multi} \text{ (app)}/K^{2/3} \quad (9)$$

The results obtained in this way are shown in Table I. The numbers for the inert gases differ slightly from those published earlier[1] because they are based on dielectric constants recalculated with recent density values[9] and polarizations.[10] The upper values correspond to K for bulk solids; at $20°K$ ($4.2°K$ for Ne) the lower ones correspond to extrapolated values for liquids. In the case of Ne and Ar the latter are almost certainly more appropriate since the layers appear definitely liquid-like in the way they flow over the emitter. Kr and Xe layers may approximate solids more closely.

The value for H_2 is based on the low branch of emission. Since emission may cause some desorption even before the switch to the high branch, i may rise more steeply than it should for pure field emission. This would increase the slope of the ln i vs. $1/V$ plot without necessarily destroying its linearity over the small range experimentally accessible, and would thus lead to a high value of ϕ. Thus 1.2 eV is an upper limit. It is possible that this explains the discrepancy between the bulk and the film results.

Table I also lists values obtained by other methods where available. The spectroscopic values for Kr and Ar by Raz and Jortner[11] are considerably lower than the field emission results, but may be subject to some uncertainty since they are based on the extrapolation to the dissociation limit of only two terms in a Rydberg series for Xe in liquid Ar or Kr, and because the polarization energy of the Xe^+ ion must be calculated rather than

(6) B. Halpern and R. Gomer, *J. Chem. Phys.*, **51**, 3043 (1969).
(7) T. Engel and R. Gomer, *ibid.*, **52**, 5572 (1970).
(8) C. Lea and R. Gomer, *ibid.*, **54**, 3349 (1971).

(9) G. L. Pollack, *Rev. Mod. Phys.*, **36**, 748 (1974).
(10) Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. 3 (II), Springer-Verlag, Berlin, 1951, p 509.
(11) See Table I, footnote *a*.

measured. Nevertheless the field-emission film values may be generally too high by 0.2–0.5 eV; this is particularly likely for Ne. This could be due in part to the low temperatures used, i.e., there could be a substantial temperature dependence of ΔH_s. There is also some uncertainty in the dielectric constants, quite apart from the question of density. The field in the layer is reduced by polarization, which should be calculated self-consistently by summation over the dipole fields from each atom. For very thin layers the sum may not build up to the bulk value but may correspond to a lower effective dielectric constant; this would reduce the heats of solution calculated from eq 9. For Kr, for example, $K = 1.5$–1.6 would be required to bring the field-emission result into agreement with that of Raz and Jortner; this is only a reduction by ~10% from the bulk liquid or ~20% from the bulk solid value. For entirely similar reasons the effective heat of solution of electrons in thin slabs may also differ from the bulk value. Since the repulsive part of this interaction is of very short range, while the attractive polarization part varies as r^{-4}, it is mainly the latter which would build up relatively slowly. This would reduce, rather than raise, film heats.

Attempts have been made to analyze field emission through layers in terms of tunneling through a potential barrier modified by the insertion of discrete atomic potentials corresponding to the adsorbed atoms. The first of these, by the author in 1959, used a very simple WKB method which is probably only qualitatively significant.[1] More recently Modinos[12] has attempted a more ambitious calculation employing a T-matrix formalism, but comes to the conclusion that even for attractive potentials there may be an increase in effective ϕ as determined from a Fowler–Nordheim slope. While it is true that there can be a reduction in overall tunneling probability even for attractive potentials, it is intuitively clear that the effective energy parameter, i.e., $\phi_{effective}$, must be coupled at least qualitatively to the location of the conduction band, which must lie below the vacuum level for an array of net attractive and above it for net repulsive potentials. The fallacy in Modinos' calculation seems to stem from his neglect of interference terms in the electron wave function which arise from back scattering by the potentials in the array.

Until more detailed calculations and experimental comparisons with other methods are available, ΔH_s from field-emission data, particularly from films, must be regarded as only semiquantitative.

Field Ionization in Liquids

The experimental technique for studying field ionization in liquids[3] is identical with that for field emission,[2] except for the inversion of polarity. For H_2 and Ar linear $\ln i$ vs. $1/V$ regimes are obtained at low currents, as required for Zener emission; the tunneling fields are typically 0.7 V/Å for H_2 and 0.5 V/Å for Ar. For N_2, only erratic and noisy emission occurs at low currents;
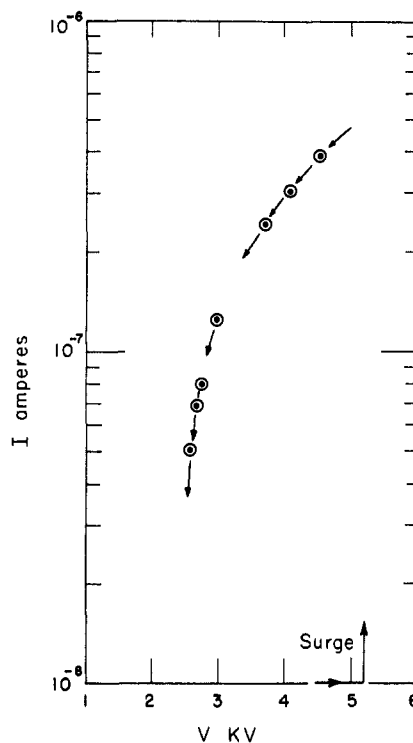
(12) A. Modinos, *Surface Sci.*, **20**, 55 (1970).

Figure 5. i vs. V for He at 4.2°K. Surge and cutoff voltages as indicated. $F/V = 2.62 \times 10^4$ cm^{-1}.

there is at present no real explanation why a good field-ionization regime is not observed. With O_2 emission sets in at 100–200 V, corresponding to tip fields of 0.04 V/Å, i.e., much too low for field ionization; emission decays rapidly and can be restored by raising the voltage; there is no tip damage. This indicates that electrochemical processes of the kind seen in field emission occur at asperities of the cathode and are responsible for the current. For He the completely reversible cycle shown in Figure 5 occurs with an onset field of 1.3 V/Å and a cutoff field of 0.64 V/Å at 4.2°K. At 1.6°K the fields are changed only slightly, but all currents for onset and cutoff are increased by ~10. There is no emitter damage, even after drawing currents as high as 10^{-5} A, indicating that there is no ion bombardment of the tip. In all systems "normal" space charge regimes occur for $i > 10^{-9}$ A.

The first thing to note is that the electrostrictive pressure increase

$$\Delta P = [(K - 1)(K + 2)/24\pi](F/300)^2 \quad (10)$$

for F in V/cm amounts to 100–500 atm at the emitter for the fields involved, and thus exceeds the solidification pressure. Since the field decreases as ~$(r_t/r)^2$ it is easy to show that the solidified zone is ~300 Å in most cases, for emitter radii of ~10^{-5} cm. It will be shown shortly that field ionization is confined to a zone of ~10 Å at the tip. Thus tunneling occurs within a solid layer; hole conduction through the solid is evidently adequate at high fields to get the charge into the liquid, whence it is carried to the cathode by positive ions. Since electron flow is confined to the ionization zone at the tip, charge multiplication by electron im-
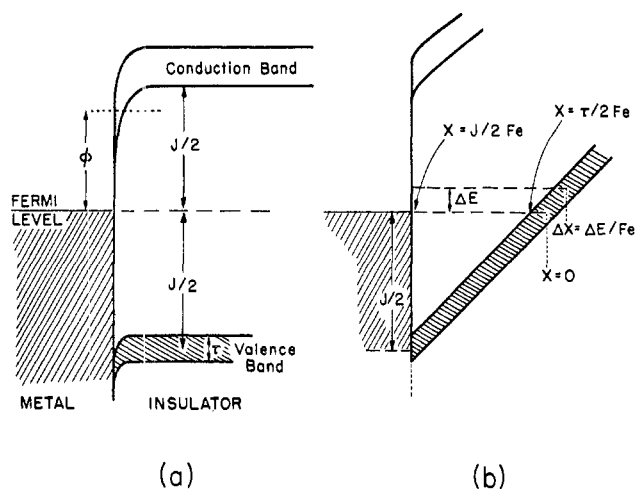
Figure 6. Diagram illustrating field ionization from an insulator whose Fermi level lies in the middle af the band gap, assuming equalization of Fermi levels of metal and insulator. Band gap, J; width of valence band, τ. (a) Situation at zero field; (b) with field F (volts/centimeter) applied.

pact cannot occur; hole conduction, which corresponds to electrons jumping to adjacent ions only, apparently does not lead to it either. These considerations explain the absence of avalanching in Ar. For He, however, charge multiplication does occur, as shown by Figure 5. The most plausible explanation is that ions in systems having either vibrational degrees of freedom or high polarizabilities can lose energy efficiently by collisions or by polaron drag, while in He ions can gain enough energy to cause ionization and thus avalanching.

Tunneling from the medium can be treated as for the atomic case if interactions in the solid are negligible. For systems like Ar a band model (Figure 6) is probably more appropriate, with tunneling considered to occur from the valence band into the metal. In the one-dimensional tight binding approximation the dispersion relation in the band is

$$E = E^{0'} - (\tau/2) \cos kd - Fex \qquad (11)$$

where $E^{0'}$ is the energy corresponding to the midpoint of the band $(x = 0)$, k the wave vector, τ the valence band width, and d the interatomic spacing. By analytic continuation into the forbidden region one can show[3] that

$$k' = (1/d) \cosh^{-1} (2Fex/\tau) \qquad (12)$$

which can now be used in the WKB expression, eq 1. The analog of x_c in the atomic model (eq 7) enters through the limits of integration $x = 0$ to $x = J/2Fe$ shown in Figure 6 which correspond to tunneling of electrons with energies greater than or equal to the Fermi level of the metal. The result, for the midpoint of the band gap at the Fermi level of the metal (i.e., for equalized Fermi levels), is

$$D(J/2) = \exp\{-(J/Fed)[\ln (2J/\tau) - 1]\} \qquad (13)$$

where J is the band gap. If vacuum rather than Fermi levels are equalized, $J/2$ must be replaced by $E^0 - \phi$ where E^0 is the absolute value of the valence band cen-

ter below the vacuum for $F = 0$. For a three-dimensional lattice, D depends on the tunneling direction. For the (111) direction of a face-centered cubic lattice, d must be replaced by $a/3^{1/2}$, a being the lattice constant.

It is easy to see that the energy parameter J in eq 13 increases for tunneling above the Fermi level and reaches a limiting value of $2J$ for interband tunneling. It is this fact which limits emission to a narrow zone near the tip and allows us to neglect entirely the body current corresponding to interband transitions. It is also easy to show that the minimum energy parameter $J/2$ will appear in the expression for total current, which is obtained by integrating the contributions from each shell, starting at x_c.

For Ar Mattheiss[13] has calculated $\tau = 0.58$ eV. If it is assumed that the conduction band is low enough to permit equalization of Fermi levels, field-ionization data give a band gap, $J = 13$ eV, in very good agreement with the calculated[13] and optical[14] values of 13 and 14 eV, respectively. However, both field emission and photoelectric data indicate, as already discussed, that the conduction band of Ar lies only 0.6–0.4 eV below the vacuum. It is thus more likely that vacuum levels are equalized. On this basis the center of the valence band would lie 16.7 eV below vacuum and the band gap would be 15.7 eV. These values are still in reasonable agreement with the calculated and optical values, since there is some uncertainty about the emission direction to choose and the actual value of τ for the tunneling calculation. For H_2, no calculation on band width exists, so that the band model is difficult to apply. If a band gap of 15 eV is chosen, $\tau = 0.12$ eV; it is reasonable to expect a very narrow valence band. For H_2, eq 5 yields an uncorrected value of $I = 11.4$ eV, while a simple perturbation calculation[3] yields 13.4 eV. The polarization energy of the ion can be estimated as ~ 1.2 eV; if the heat of solution of electrons is -0.5 eV, these results become 12 and 14 eV, respectively, in reasonable agreement with the gas-phase value of 15.6 eV. It is clear from these results that well-defined electrode systems of the type employed here yield remarkably good energy parameters for tunneling and leave little doubt of the validity of the tunneling mechanism.

Space Charge and Mobilities

We have already alluded to space-charge regimes at sufficiently high currents in bulk liquids. The space-charge equations (for specificity negative charge carriers are assumed for the moment) can be derived by combining Poisson's equation (eq 14) and the equation for

$$\nabla^2 V = 4\pi\rho/K \qquad (14)$$

charge density (eq 15) with an appropriate expression

$$\rho_- = i_-/\gamma\pi r^2 v \qquad (15)$$

for the velocity of charge carriers in terms of V or dV/dr. In gases where $(1/2)mv^2 = eV$, the well-known

(13) L. F. Mattheiss, Phys. Rev. A, 133, 1399 (1964).
(14) G. Baldini, ibid., 128, 1562 (1962).

Table II

Mobilities

Substance	$\mu-(FE)^i$	$\mu-$(other)	μ_+(FI)	μ_+(other)
H$_2$, 20.4°K	$3 \pm 1 \times 10^{-2}$		4.5×10^{-2}	
D$_2$, 20.4°K	$9 \pm 3 \times 10^{-3}$			
He, 4.2°K	$4 \pm 2 \times 10^{-2}$	0.0216;[a] 0.0194[b]	0.13	0.1;[e] 0.053;[a] 0.048[b]
He, 1.6°K	0.36 ± 0.1	0.200;[c] 0.174[b]	0.60	0.2;[e] 0.11;[f] 0.244[b]
O$_2$, 90°K	$8 \pm 3 \times 10^{-3}$		8×10^{-3}	
N$_2$, 77°K	$8 \pm 4 \times 10^{-3}$; 10^{-3} [d]		10^{-2}	2×10^{-3} [g]
Ar, 85°K			$8.5 \pm 1.5 \times 1^{-3}$	2.8×10^{-3};[e] 7×10^{-4} [g,h]

[a] Reference 15. [b] K. W. Schwarz (unpublished). [c] Reference 16. [d] Reference 17 (by a field emission technique). [e] Reference 18. [f] Reference 19. [g] Reference 20. [h] Reference 21. [i] All values in cm^2 volt^{-1} sec^{-1}; FE = field emission; FI = field ionization.

$V^{3/2}$ relation results. In liquids, for constant mobility, $v = \mu F$, it can be shown[2] that

$$V = V_{vac} + 2(8R/3\gamma\mu K)^{1/2}i^{1/2} \qquad (16)$$

for concentric spherical electrodes where V is the applied voltage, R is the radius of the outer electrode, and $\gamma\pi$ is the solid angle into which emission occurs. V_{vac} is the voltage which would produce the observed current if there were no space charge effects; for field emission and ionization it would thus provide the actual tip field if there were no space charge. A pure field emission regime occurs when the second term in eq 16 is negligible relative to V_{vac}. For V in volts, i in nanoamperes, R in centimeters, and μ in cm^2 sec^{-1} volt^{-1} eq 16 takes the form

$$V = V_{vac} + 98(R/K\mu\gamma)^{1/2}i^{1/2} \qquad (17)$$

Equations 16 and 17 are strictly true only for $\gamma = 4$; since space-charge spreading can be shown to be small, they should be reasonable approximations for actual geometries, $\gamma \sim 0.6$. The validity of eq 16 is not restricted to current generation by field emission or ionization, but applies also to charge multiplication in the liquid or in a gas bubble, as long as the source region is well defined and charge multiplication does not occur beyond it. If current (in the absence of space charge) varies much more rapidly with V_{vac} than it does with V, which is certainly true for field emission and ionization and also for avalanches and discharges, V_{vac} will remain virtually constant over the range of a space-charge plot so that V will vary linearly with $i^{1/2}$, as observed.

It might seem questionable at first sight to expect constant mobility in view of the high fields near the tip. It can be shown, however, that space charge effects arise from charge accumulation at $r \gg r_t$, where the field is quite low, and that μ in eq 16 refers to these regions. Unlike the vacuum case, however, the field is not negligible even at the outer electrode but is given there[2] by eq 18, so that the mobilities in eq 16 refer to

$$F_{outer} = (8i/3\gamma K\mu)^{1/2}R^{-1/2} \qquad (18)$$

$F \sim 500$ V/cm for negative and ~ 1000 V/cm for positive charge carriers.

The results for liquids obeying eq 16 are summarized in Table II together with values obtained by other methods where available.[15-21] The agreement with the latter is generally fair; field-emission and ionization re-

sults tend to be somewhat higher than values from other methods. This may be due to the oversimplified geometry used in deriving eq 16 and also to the fact that liquid motion, caused by viscous drag of the carriers, has been neglected. It is probable that calibration with liquids of known mobility to take care of geometric factors would make it possible to obtain very accurate values simply and quickly, since the field-emission method is inherently much simpler than most other ones.

The results listed in Table II show that the low-field mobilities of negative and positive charge carriers are almost the same in liquids like O$_2$ where electron attachment occurs, i.e., where the conduction mechanism is very similar (ion drift and charge hopping). For H$_2$ and He, where electrons are believed to dig bubbles, the negative mobilities are, in fact, smaller than those of the positive ions. In no case so far discussed is there evidence of free-electron conduction. It should be emphasized again that these conclusions apply to low-field regions far from the tip and have no bearing on the situation in the very high-field region there. It is certain that tunneling involves only free electrons, as already pointed out. It is also very likely that bubble formation occurs only after electrons have moved considerable distances, enough in the case of He, for instance, to cause avalanching.

For electrons in Ar the situation is radically different from that so far described. Equation 16 is not obeyed; instead $i \propto V$ even at very high currents. If the assumption of constant mobility is replaced by that of constant velocity, independent of field, the analog to eq 16 becomes

$$V = (4i/\gamma Kv)[\ln (R/r_t) - 1] + V_{vac} \qquad (19)$$

On this basis velocities of $2-5 \times 10^5$ cm/sec can be calculated for direct current and as high as 5×10^6 cm/sec for microsecond pulse regimes (where voltages and fields are correspondingly higher). It can be shown that such velocities in fact occur. If average current is plotted as function of pulse width, τ_p, a linear curve extrapolat-

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ing to the origin is observed for $\tau_p \geq 2 \, \mu\text{sec}$. This indicates that the transit time of electrons is much less than the pulse width, *i.e.*, that velocities of $\sim 10^6$ cm/sec occur. By contrast, current is quite independent of pulse width for Ar^+ ions, whose transit times are much longer. One is thus forced to the very surprising conclusion that electrons in Ar, once accelerated to a certain velocity in the high-field region near the tip, can coast through distances of the order of 2–5 mm without being appreciably slowed down. At present no convincing theoretical explanation is available. If unpurified Ar containing some O_2 is used, perfectly normal space-charge behavior occurs, because of trapping by the impurities. To date such doping experiments have not been carried out systematically.

Field Ionization from Films

It is also possible to observe field ionization from the edges of films. These may be "naturally" occurring multilayers or, for substances of high polarizability, α, or permanent dipole moment, P, they may be field induced.[22] In the latter case the field energy, $\frac{1}{2}\alpha F^2 + PF$, may be sufficient to permit film formation at very low pressures even at room temperature. This is observed with H_2O and many organic molecules and leads to interesting chemical effects, which can be studied mass spectrometrically.[22] Thus water polymers, polymerization reactions, and so on can be observed.[23] The ionization fields for films are usually $\sim 1/2$ those required for true gas-phase ionization because of the long dwell time of the molecules in the ionization zone, as can be verified, for weak adsorption, by raising T slightly. The details of the ionization mechanism from films can be quite complicated, however, and depend *inter alia* on the film thickness. The latter is determined by the balance of gas supply to the tip and loss from it. The loss rate is the sum of the evaporation rate (a function of the field-dependent adsorption energy) and the ionization rate.

$$-\frac{dn}{dt} = \pi r^2 \left[\rho/\tau_t + p_0 (2\pi m k T)^{-1/2} \times \right.$$

$$\left. \exp\left(\frac{1}{2}\alpha F^2(r) + Q(r) + PF(r) \right) \Big/ kT \right] \quad (20)$$

Here p_0 is the vapor pressure, $Q(r)$ is the distance-dependent difference between the adsorption energy and the heat of vaporization, ρ is the surface density of ionizable species, and τ_t^{-1} is the ionization frequency, which is 0 for $x < x_c$ and which decreases rapidly from its maximum value at x_c for larger distances. Since $F(r) \approx F_t(r_t/r)^2$, both Q and the field-dependent part of the adsorption energy vary with distance from the tip surface; the film thickness is thus determined by the intersection of the loss rate *vs.* distance curve with the (essentially horizontal) supply *vs.* distance curve which is in first order a function only of T and p. If the ionization rate is low, it may happen

that the film thickness $x_f > x_c$. Under these conditions ionization can occur within the film, but the rate-determining step may be the evaporation of the ion (thermally or by tunneling) from the film edge. This seems to occur for H_2 at $4.2°K$ and $p = 2 \times 10^{-7}$ Torr.[24] If the field is raised, *i.e.*, the ionization rate sufficiently increased, the film will get thinner until $x_f = x_c$; at that point current will become supply limited. On the other hand, for some set of conditions $x_f < x_c$ it may happen that an increase in F to the point where $x_f = x_c$ does not lead to a high ionization probability; under these circumstances ionization may be rate limiting. Thus the chance of observing an ionization-limited regime is greatest for naturally thin films; in fact, such a regime can be observed for He under conditions where this is true.[25] If F is increased sufficiently the ionization probability can always be made high enough, of course, to make current supply limited. It turns out that for gases like H_2 or He at least, and probably even for polar substances, supply then occurs by impingement on the emitter shank, followed by diffusion to the ionization zone. The length of the supply zone is $\sim(D_s t)^{1/2}$, where D_s is the surface diffusion coefficient of the migrating species and t is a critical time; for sparse coverage (*i.e.*, weak adsorption), t is the mean life with respect to evaporation; for high coverage (*i.e.*, long life on the surface), it is the layer replenishment time. The first regime makes i proportional to gas pressure p; the second yields $i \propto p^{1/2}$. For He films both regimes can be observed under suitable conditions.[25] Apart from its intrinsic interest, ionization from films provides high-intensity point sources of ions at much lower pressures than is possible for gas-phase ionization. The trick consists of cooling the tip to the point where film formation occurs, but where D_s is still adequate to make the supply length ~ 0.01 cm.

Concluding Remarks

The foregoing has given a rather brief look at some of the phenomena which can be studied by field emission and ionization in condensed phases. Many of these, for instance, electronic heats of solution and mobilities of charge carriers, can undoubtedly be studied more accurately, and over a wider range of well-defined parameters by other methods, but the techniques described here give an overview of all these properties. Field emission and ionization have some unique features: electrodes can be made atomically perfect, if necessary, and can be examined with almost atomic resolution by field-emission or field ion microscopy after experiments in liquids; they provide well-defined geometries and accurately known fields up to several volts per ångström; they are high-current electron and ion sources in liquids, and high-current point sources of ions or electrons in the gas phase. It is to be hoped that some of these useful properties will be more fully exploited for the study of chemical systems.

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