CHARGE TRANSFER UPON CONTACT BETWEEN METALS AND INSULATORS

by

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AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
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The equilibrium charge distribution between substances in contact has been calculated for several cases in the one-dimensional approximation, e.g. metal-insulator, metal-semiconductor, and metal-metal. In addition to these cases, we have considered insulator-insulator contacts, and certain other metal-insulator contacts. The direction of charge transfer is, of course, such as to equalize the Fermi levels. The order of magnitude of the charge and of the effective depth of the charged regions depend on the relative positions of the energy bands in contact. Thus, for example, in the metal-insulator case it is possible to have either a large charge density (10^{11} statcoulombs/cm^3) in a thin layer (10^{-8} cm), or small charge density (10^{-1} statcoulombs/cm^3) in a thick layer (10^{-2} cm). The insulator-insulator cases give rise to similar distributions. The energy levels in most insulators are too poorly known to permit strict quantitative comparison with experiment, but the results permit a semi-quantitative explanation of many of the observations in static electrification. The calculations were carried out assuming the bodies in immediate contact. No consideration was given the problem of a dielectric gap separating the bodies.

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Donald Van Ostenburg

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CHAPTER I

INTRODUCTION

Contact phenomena play an important role in present-day physics. It is convenient to make a division into time-dependent and time-independent processes. Under the time-dependent type we have, for example, the point contact and the junction transistor where charge flows in more or less steady fashion. Under the time-independent type we have the phenomena of contact potentials and static electrification. This paper is concerned with only the last process.

We have made an attempt to explain some results of static electrification as reported by Hersh and Montgomery[1] and by Harper[2]. Various authors have calculated the equilibrium charge distribution between substances in contact for several cases in the one-dimensional approximation, e.g. metal-insulator[3], metal-semiconductor[3,4], metal-metal[4]. Besides these cases we have considered insulator-insulator contacts and certain additional metal-insulator contacts. The direction of charge transfer is, of course, such as to equalize the Fermi levels. The order of magnitude of the charge and of the effective depth of the charged region depends on the relative position of the energy bands in contact. Assuming an energy-band structure for the substances, we have determined the sign of the charge transferred the charge density, field strength, and potential variation with distance in the materials. The calculations are carried out by applying Fermi-Dirac statistics in order to find the charge density. We then solve Poisson's equation in each region and match the solutions at the boundary by means of suitable boundary conditions. This procedure gives us the necessary conditions to determine the constants and, therefore, permits solution of the problem. The calculations show that ample charge is transferred to explain some experimental data and so in these cases it is unnecessary to invoke surface states or local heating. The calculations were carried out assuming the bodies in immediate contact, the interpenetration of the bodies being supposed deep enough so that the interior structure need only be considered. No consideration was given the problem of a dielectric gap separating the bodies, although it is believed that this will have an appreciable effect in reducing the magnitude of charge transferred.

CHAPTER II

PROPERTIES OF ELECTRONS IN SOLIDS, CHARGE DENSITY, AND ELECTRICAL CONTACTS

A. Electrons in Solids [5]

The first theory of electrons in solids was given in 1900 by Drude. He assumed that electrons in a metal were free and form an electron "gas" in a container. This simple model predicts the law of Wiedemann and Franz that the ratio of the thermal conductivity K to the electrical conductivity σ is proportional to the absolute temperature T. In addition the value of the Lorentz number $L \equiv K/\sigma T$ was in good agreement with experimental data. However, the temperature dependence for the electrical and thermal conductivities treated separately was in error. Lorentz extended the theory using Maxwell – Boltzmann statistics in a more detailed consideration of the collision phenomena. The results explained the Wiedemann--Franz law, but again failed to give the correct temperature dependence of the conductivities. Also the theory indicated that in connection with the mean free path of electrons there should be one free electron for each atom of the metal. If this were true it would lead to unusually large values for the specific heat of metals as compared with insulators, in contradiction with the law of

DuLong and Petit. Eventually Sommerfeld[6] applied Fermi-Dirac statistics, and resolved the difficulty of the specific heat, but the predicted value of the conductivity was still not in good agreement with experiment unless free paths of the order of a hundred interatomic units were assumed. At that time there was no reason to expect such large free paths. In 1928, W. V. Houston[7] showed that an electron in a perfect crystallattice can move unhindered throughout the crystal. In reality there are lattice imperfections, in the form of vibrations and impurities, which cause a finite free path. The concepts of quantum mechanics show that when isolated atoms combine to form a solid the discrete energy levels of an electron broaden into a band structure. Wilson[8] in 1931 used these ideas to explain the difference between a metal and an insulator. Quantum mechanical calculations show that for nearly free and for tightly bound electrons the dependence of energy on the propagation vector k can be placed in the form[ref.5,p.43]

$$(1) \qquad E = \frac{1}{2}\frac{\hbar^2 k^2}{m^*} \qquad \text{(nearly free)}$$

$$(2) \qquad E = A - \frac{1}{2}\frac{\hbar^2 k^2}{m^*} \qquad \text{(tightly bound),}$$

where m^* is the effective mass of the electron and in (2) A is the energy at the top of the band; $\hbar$ is Planck's constant divided by 2π. When the energy of an electron is given by (1) we have a <u>normal energy band of standard form</u>. It represents the behavior of nearly free electrons (and in addition tightly bound electrons near the bottom of an energy band). When the energy is given by (2), we have an *inverted band of standard form*. It represents the behavior of tightly bound electrons near the top of an energy band. If we take into account the exchange energy the term[9]

$$\frac{e^2}{2\pi}\left\{2k_m + \frac{k^2-k_m^2}{k}\ln\frac{|k_m-k|}{k_m+k}\right\}$$

must be subtracted from (1) and (2), k_m being the magnitude of the propagation vector corresponding to maximum energy, and e the electronic charge. The exchange energy has this form when the electrons are perfectly free and are considered as a degenerate Fermi gas filling all states up to a maximum level with two electrons of opposite spin.

The calculations that we wish to make require a knowledge of the electron charge density. This in turn depends upon the density of electronic states into which electrons may enter. Hence, we discuss the density of electronic states.

B. Charge Density

The volume of phase space occupied by N electrons confined to a spatial volume V and occupying a volume in momentum space dp is $V dp$ [10]. Quantum statistical mechanics tells us that the volume of the smallest cell in phase space associated with an electron of given spin direction is equal to h^3. The number of cells is therefore given by $V dp / h^3$. We define $n(E)dE$ to be the number of energy levels per unit volume (for one direction of electron spin) lying in the range dE at E. This gives $n(E)dE = d\mathbf{p}/h^3$. Expressing $\mathbf{p}$ in terms of the propagation vector $\underline{k}$ we have, since $\mathbf{p} = \hbar \underline{k}$,

$$n(E)dE = \frac{1}{8\pi^3}\, d\underline{k}.$$

For free electrons $\underline{k}$-space fills up with spherical symmetry and so the volume in $\underline{k}$-space contained between two concentric spheres of radii k and k + d k is $4\pi k^2 dk$; and $d\underline{k} = 4\pi k^2 dk$.

Thus,

$$n(E)dE = \frac{4\pi k^2 dk}{8\pi^3} = \frac{1}{2\pi} k^2 dk.$$

Substituting from (1) and (2) the value of k in terms of E, we have for the density of states for bands of standard and inverted form respectively,

$$(3)\quad n(E)dE = \frac{1}{4\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE = 2\pi\left(\frac{2m^*}{h^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}} dE,$$

$$(4)\quad n(E)dE = \frac{1}{4\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} (A-E)^{\frac{1}{2}} dE = 2\pi\left(\frac{2m^*}{h^2}\right)^{\frac{3}{2}} (A-E)^{\frac{1}{2}} dE.$$

If each allowed state were occupied by an electron we would integrate the proper expression for the density of states over the required energy region in order to determine the number density of electrons in that range. Electrons, however, obey Fermi-Dirac statistics, and we must multiply the density of states by the Fermi-Dirac distribution function, given by

$$f(E) = \frac{1}{e^{(E-\zeta)/kT} + 1},$$

where E is the energy of the state in question and ζ the Fermi level. Here k is Boltzmann's constant, and T again the absolute temperature. The number density of electrons in a range (a, b) is given by an expression of the form

$$\int_a^b n(E) f_-(E)\, dE \ .$$

Multiplying the number density by the charge on the electron gives the charge density. These concepts will be applied in the next and later chapters where we consider in detail the charge distribution at contacts.

C. Basic Properties of Contacts

As is well known, when two bodies are placed in contact charge tends to flow so as to equalize their Fermi levels. This give rise to charge layers of opposite sign in the two bodies. In Figures 1, 2, 4, 5, 6, 7, and 8 we see energy level diagrams of bodies before and after contact. Before contact the levels are shown constant up to the edge of the crystal. After contact, as a result of the transferred charge, the potential energy of an electron within the crystal will change, the levels shifting accordingly. The total shift from one substance to the next is e $(\Delta V_1 - \Delta V_2)$, where ΔV_1 is the total shift in the electrostatic potential of an electron in the substance on the left and ΔV_2 the corresponding quantity for the substance on the right.

In the insulator we are concerned with the energy χ_0 released when an electron at rest outside the crystal is taken into the lowest level in the uppermost nearly empty band. This quantity is the analog of the electron affinity A for a free molecule. We are concerned also with the energy ν_0 necessary to remove an electron from the highest level of the uppermost nearly filled band. This quantity is the analog of the ionization potential I for a free molecule. The quantity χ_0 is usually called "electron affinity" in solid state literature, but we prefer some designation differentiating it from the quantity A for a free molecule. The quantity ν_0 does not seem to have been called "ionization potential," however, the reasons for such a designation are just as good as those for "electron affinity." At present we do not wish to introduce a new terminology, nor continue to use what to us is undesirable, and so shall try to get by with the use of symbols only. In the metal we are concerned with the energy ϕ_0 released when an electron at rest outside the crystal is taken to the Fermi level, or absorbed when an electron is taken from the Fermi level to a point outside the crystal. In a sense ϕ_0 may be considered the analog of either the electron affinity or the ionization potential for a free molecule. It has been given the special name, work function. We are also concerned with the energy of an electron at the bottom of the half-filled band in the metal and designate this by ω_0 .

In the figures the energy parameters of the substance on the left contain the subscript one, and the substance on the right contain the subscript two; For example, Figure 1 represents a metal-metal contact in which the charge flows from metal 2 to metal 1. As a result the levels in 1 are shifted upward by an amount $e\Delta V_1$ while those in 2 downward an amount $e\Delta V_2$. Near the contact the energy of an electron is not constant, and so the variation is designated by ω_1 and ω_2 in the two metals respectively. The reference level is taken with respect to the shifted levels. In contacts involving insulators we take χ_2 and V_2 to indicate variable energy parameters. Further details are given in the remaining chapters of this paper.

CHAPTER III

METAL-METAL CONTACTS

A. Charge Density in the Metal

Owing to the large density of states of a metal we would expect the transferred charge to reside in a small spatial region. Suppose the metals placed in contact have the relative energy band structure shown in Figure 1. Electrons flow from right to left causing the metal on the left to become negatively charged, the one on the right positively charged.

To see in more detail the charge distribution and potential energy variation we turn to a discussion of the net charge density and solve Poisson's equation for the potential.

The electron charge density is

$$\rho_{1-}(x) = -2e\int_{-\infty}^{\infty} f_-(E)\,n_-(E)\,dE = -2e\int_{-\infty}^{\omega_1+e\Delta V_1} f_-(E)\,n_-(E)\,dE - 2e\int_{\omega_1+e\Delta V_1}^{\infty} f_-(E)\,n_-(E)\,dE,$$

and the positive charge density is

$$\rho_{1+}(x) = +2e\int_{-\infty}^{\infty} f_+(E)\,n_+(E)\,dE = 2e\int_{-\infty}^{\omega_1+e\Delta V_1} f_+(E)\,n_+(E)\,dE + 2e\int_{\omega_1+e\Delta V_1}^{\infty} f_+(E)\,n_+(E)\,dE,$$

$f_+(E)$ being a distribution function for the positve charge. It is a step function

$$f_+(E) = \begin{cases} 0 & \infty > E > \zeta \\ 1 & \zeta > E > \omega_1 + e\Delta V_1 \end{cases}.$$

The factor 2 accounts forthe two directions of spin. Assuming that electrons are not excited out of the lower bands in the metal, the first terms in each expression for $\rho_1(x)$ are equal but of opposite sign. Insofar as the electrons in a metal form a degenerate gas[11] even at room temperature, we may replace $f_-(E)$ by the step function

$$f_-(E) = \begin{cases} 0 & \infty > E > \zeta \\ 1 & \zeta > E > \omega_1 + e\Delta V_1 \end{cases} .$$

Combining the two expressions substituting the values of $f(E)$, the net total charge density in the metal is

$$\rho_1(x) = -2e\int_{\omega_1+e\Delta V_1}^{\infty} f_-(E)n_-(E)dE + 2e\int_{\omega_1+e\Delta V_1}^{\infty} f_+(E)n_+(E)dE$$

$$= -2e\int_{\omega_1+e\Delta V_1}^{\zeta} n_-(E)dE + 2e\int_{\omega_1+e\Delta V_1}^{\zeta} n_+(E)dE$$

The integral $\int_{\omega_1+e\Delta V_1}^{\zeta} n_+(E)dE$ represents the number density of positive charge. This is constant before and after contact (no ionic current); therefore, we can change the lower limit to $\omega_{01}+e\Delta V_1$.

We get, using (3) p. 6,

$$\rho_1(x) = -4\pi\left(\frac{2m^+}{h^2}\right)^{\frac{3}{2}} e\int_{\omega_1+e\Delta V_1}^{\zeta}\left[E-(\omega_1+e\Delta V_1)\right]^{\frac{1}{2}}dE + 4\pi\left(\frac{2m^+}{h^2}\right)^{\frac{3}{2}} e\int_{\omega_{01}+e\Delta V_1}^{\zeta}\left[E-(\omega_{01}+e\Delta V_1)\right]^{\frac{1}{2}}dE .$$

We take $n_+(E) = n_-(E)$ because we look at $n(E)$ as a density of states for numbers of particles. Changing variables in each integral to $\lambda = E - (\omega_1 + e\Delta V_1)$ and $\lambda = E - (\omega_{01} + e\Delta V_1)$, respectively, we have

$$\rho_1(x) = 4\pi \left(\frac{2m^*}{h^2}\right)^{\frac{3}{2}} e \left\{ - \int_0^{\zeta - (\omega_1 + e\Delta V_1)} \lambda^{\frac{1}{2}} d\lambda + \int_0^{\zeta - (\omega_{01} + e\Delta V_1)} \lambda^{\frac{1}{2}} d\lambda \right\}$$

$$= \frac{8\pi}{3} \left(\frac{2m^*}{h^2}\right)^{\frac{3}{2}} e \left\{ \left[\zeta - (\omega_{01} + e\Delta V_1)\right]^{\frac{3}{2}} - \left[\zeta - (\omega_1 + e\Delta V_1)\right]^{\frac{3}{2}} \right\}.$$

This expression represents the net charge density in metal 1 as an intrinsic function of distance, the distance occurring in the variable $\omega_1(x)$. We are now ready to compute the potential energy variation of an electron in the metal by means of Poisson's equation.

B. Solution of Poisson's Equation

We are to solve

$$\frac{d^2V}{dx^2} = - \frac{4\pi}{\varepsilon_1} \rho_1(x),$$

where V is the electrostatic potential and ε_1 the dielectric constant of free space. Substituting the charge density derived in A we see

$$\frac{d^2\omega_1}{dx^2} = K_1\left\{\left[\zeta-(\omega_{01}+e\Delta V_1)\right]^{\frac{3}{2}} - \left[\zeta-(\omega_1+e\Delta V_1)\right]^{\frac{3}{2}}\right\},$$

where $K_1 = \frac{32\pi^2e^2}{3\epsilon_1}\left(\frac{2m^*}{h^2}\right)^{\frac{3}{2}}$, and $\omega_1 = -eV$,

ω_1 being the potential energy of an electron.

Let $y_1 = \zeta-(\omega_1+e\Delta V_1)$,

$y_{01} = \zeta-(\omega_{01}+e\Delta V_1)$;

and then,

$$\frac{d^2y_1}{dx^2} = K_1\left\{ y_1^{\frac{3}{2}} - y_{01}^{\frac{3}{2}}\right\}.$$

Placing

$$\frac{d^2y_1}{dx^2} = \frac{1}{2}\frac{d}{dy_1}\left(\frac{dy_1}{dx}\right)^2,$$

$$\frac{1}{2}\frac{d}{dy_1}\left(\frac{dy_1}{dx}\right)^2 = K_1\left\{ y_1^{\frac{3}{2}} - y_{01}^{\frac{3}{2}}\right\}.$$

Integrating from $y_1(x)$ to y_{01}; the value of y_1 where $x \to -\infty$;

$$\frac{1}{2}\int_0^{\frac{dy_1}{dx}}\frac{d}{dy_1}\left(\frac{dy_1}{dx}\right)^2 dy_1 = K_1\int_{y_{01}}^{y_1(x)}\left\{ y_1^{\frac{3}{2}} - y_{01}^{\frac{3}{2}}\right\}dy_1;$$

$$\frac{1}{2}\left(\frac{dy_1}{dx}\right)^2 = K_1\left\{\frac{2}{5}y_1^{\frac{5}{2}} - y_{01}^{\frac{3}{2}}y_1\right\}_{y_{01}}^{y_1(x)}$$

$$= K_1 \left\{ \frac{2}{5} y_1^{\frac{5}{2}} - y_{01}^{\frac{3}{2}} y_1 - \frac{3}{5} y_{01}^{\frac{5}{2}} \right\};$$

$$\left(\frac{dy_1}{dx}\right)^2 = K_1 \left\{ \frac{4}{5} y_1^{\frac{5}{2}} - 2 y_{01}^{\frac{3}{2}} y_1 - \frac{6}{5} y_{01}^{\frac{5}{2}} \right\}$$

$$= K_1 y_{01}^{\frac{5}{2}} \left\{ \frac{4}{5} \left(\frac{y_1}{y_{01}}\right)^{\frac{5}{2}} - 2 \left(\frac{y_1}{y_{01}}\right)^{\frac{3}{2}} - \frac{6}{5} \right\}.$$

Now $\Delta y_1 = y_1 - y_{01} = \omega_{01} - \omega_1,$

$$\frac{y_1}{y_{01}} = \frac{y_{01} + \Delta y_1}{y_{01}} = 1 + \frac{\Delta y_1}{y_{01}} = 1 + \gamma,$$

where $\gamma = \Delta y_1 / y_{01}$.

Our equation becomes

$$\left(\frac{dy_1}{dx}\right)^2 = K_1 y_{01}^{\frac{5}{2}} \left\{ \frac{4}{5} (1+\gamma)^{\frac{5}{2}} - 2(1+\gamma) + \frac{6}{5} \right\}.$$

Since for a metal $\frac{\Delta y_1}{y_{01}} \ll 1,$ we may expand the first term, obtaining

$$\left(\frac{dy_1}{dx}\right)^2 = K y_0^{\frac{5}{2}} \left\{ \frac{4}{5} \left(1 + \frac{5}{2}\gamma + \frac{5}{2}\,\frac{3}{2}\,\frac{1}{2}\gamma^2 + \cdots\right) - 2(1+\gamma) + \frac{6}{5} \right\}$$

$$= K y_{01}^{\frac{5}{2}} \frac{3}{2} \gamma^2,$$

neglecting higher order terms.

But $y_1 = y_{01} + \Delta y_1$

and $\frac{dy_1}{dx} = \frac{d\Delta y_1}{dx},$

so $$\left(\frac{d(\Delta y_1)}{dx}\right)^2 = \frac{3}{2} K_1 y_{01}^{\frac{5}{2}} \left(\frac{\Delta y_1}{y_{01}}\right)^2 = \frac{3}{2} K_1 y_{01}^{\frac{1}{2}} (\Delta y_1)^2,$$

and $$\frac{d\Delta y_1}{dx} = \sqrt{\frac{3}{2} K_1 y_{01}^{\frac{1}{2}}}\, (\Delta y_1).$$

where we must take the positive sign. Integrating from $x = 0$ to x,

$$\int_{\Delta y_1(0)}^{\Delta y_1(x)} \frac{d(\Delta y_1')}{\Delta y_1'} = \sqrt{\tfrac{3}{2} K\, y_{01}^{\frac{1}{2}}} \int_0^x dx',$$

$$\ln \Delta y_1' \Big|_{\Delta y_1(0)}^{\Delta y_1(x)} = \sqrt{\tfrac{3}{2} K_1\, y_{01}^{\frac{1}{2}}}\; x,$$

$$\frac{\Delta y_1(x)}{\Delta y_1(0)} = e^{\sqrt{3/2\, K_1\, y_{01}^{1/2}}\; x}.$$

Now $\Delta y_1(0) = y_1(0) - y_{01}(0) = e\,\Delta V_1$, a positive quantity:

$$y_1 - y_{01} = \Delta y_1(x) = -(\omega_1 - \omega_{01}).$$

Thus,

$$\omega_1 - \omega_{01} = -e\,\Delta V_1\, e^{\sqrt{\frac{3}{2} K_1\, y_{01}^{\frac{1}{2}}}\; x}.$$

Defining $\ell_1 = \dfrac{1}{\sqrt{3/2\, K_1\, y_0^{1/2}}}$, we have

$$\text{(5)} \qquad \omega_1 - \omega_{01} = -e\,\Delta V_1\, e^{\frac{x}{\ell_1}}. \qquad (x \leq 0)$$

We proceed in exactly the same manner to find the charge density and potential energy variation in metal 2. We find that

$$\omega_2 - \omega_{02} = -e\,\Delta V_2\, e^{-\frac{x}{\ell_2}} \quad (x \geq 0) \quad \text{and} \quad \ell_2 = \frac{1}{\sqrt{\frac{3}{2} K_2\, y_{02}^{1/2}}},$$

where $e\,\Delta V_2$ is negative, and the negative sign in the exponent is used since x is positive.

To evaluate the unknowns $e\Delta V_1$, $e\Delta V_2$, and ζ, we match the two solutions at the boundary by means of the condition that the field strength must be continuous across the boundary, and that at infinity $\omega_{01} + e\Delta V_1 + y_{01} = \zeta$ and $\omega_{02} + e\Delta V_2 + y_{02} = \zeta$

These conditions give respectively $\dfrac{\Delta V_1}{\Delta V_2} = -\dfrac{\ell_1}{\ell_2}$,

and $\omega_{01} + e\Delta V_1 + y_{01} = \omega_{02} + e\Delta V_2 + y_{02}$,

or $\phi_{01} + e\Delta V_1 = \phi_{02} + e\Delta V_2$.

If we assume the effective mass to be the same in metal 1 as in 2, and $\varepsilon_1 \simeq \varepsilon_2$; then $K_1 \simeq K_2$,

and $\dfrac{\Delta V_1}{\Delta V_2} \simeq -\sqrt{\dfrac{y_{02}^{1/2}}{y_{01}^{1/2}}}$

Taking $y_{01} = 2$ e.v., $y_{02} = 3$ e.v., $\phi_{01} = -6.23$ e.v., $\phi_{02} = -4$ e.v.,

$$\frac{e\Delta V_1}{e\Delta V_2} = -1.11$$

$$e\Delta V_1 - e\Delta V_2 = \phi_{02} - \phi_{01} = 2.23,$$

$$e\Delta V_2 = -1.055,$$

$$e\Delta V_1 = 1.172, \qquad \ell_1 = .68 \times 10^{-8}\ \text{cm}$$

and $\zeta = \omega_{01} + e\Delta V_1 + y_{01} = \phi_{01} + e\Delta V_1 = -5.05$ e.v.,

If the energy bands are such that the Fermi level in metal 1 is above that of metal 2 the charge flows in the opposite direction. The calculations proceed in exactly the same manner.

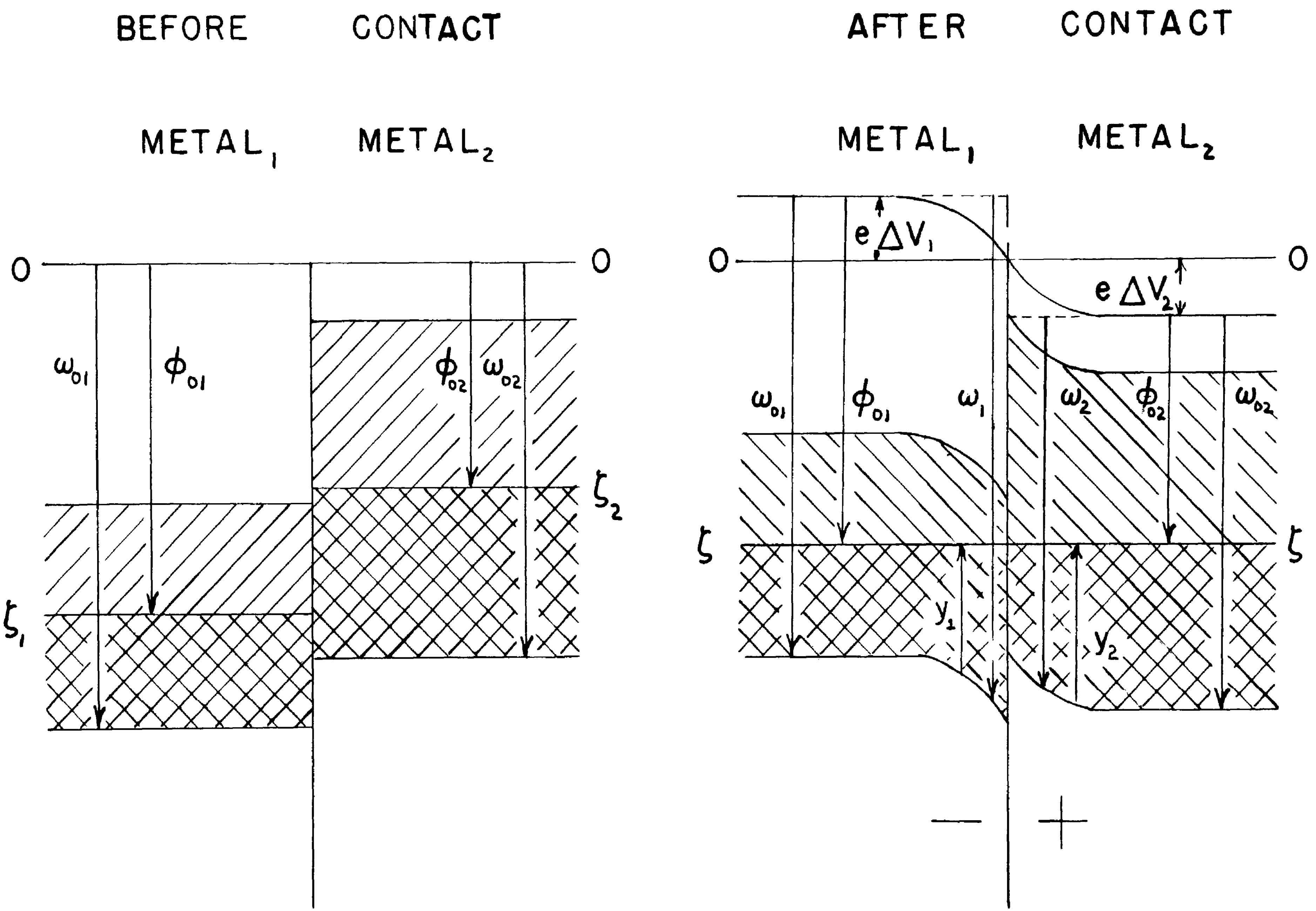

Figure 1. Schematic Energy-Band Diagram: Metal-Metal Contact

CHAPTER IV

METAL-INSULATOR CONTACTS

A. General Behavior

We now consider four cases of metal-insulator contacts. Figure 2 represents the contact between a metal and an insulator when before contact the Fermi level in the metal lies above the Fermi level in the insulator, and when the Fermi level in the metal lies above the bottom of an empty band in the insulator. Then electrons can spill from the half-filled band in the metal into the empty band in the insulator. Hence, large charge is lost by the metal from a small spatial region, and a large amount gained by the insulator within a small spatial region.

Figure 4 is the case where before contact the Fermi level in the metal lies below the Fermi level in the insulator and where the top of a filled band of the insulator lies above the Fermi level in the metal. Electrons can spill from the filled band in the insulator to the half-filled band in the metal. Much charge is lost by the insulator from a small spatial region, and much gained by the metal within a small spatial region.

Figure 5 is the case discussed by Mott and Gurney[3] when in isolation the Fermi level in the metal lies above the Fermi level in the insulator, and when the bottom of the empty band of the insulator lies above the Fermi level in the metal. Electrons escape by thermal agitation from the filled band in the metal to the empty band of the insulator. Small charge is lost by the metal in a small spatial region and the same amount gained by the insulator in a large spatial region.

Figure 6 represents the contact when in isolation the Fermi level in the metal lies below the Fermi level in the insulator, and when the top of the filled band of the insulator lies below the Fermi level in the metal. Electrons escape from the insulator only by thermal agitation from the filled band in the insulator to the half-filled band in the metal. Small charge is lost by the insulator from a large spatial region and an equal charge gained by the metal within a small spatial region. Calculations which verify these statements are made in the remaining portion of this chapter.

B. Case of Large Charge Transfer from Metal to Insulator

From Figure 2 we see that the electron charge density in the insulator is given by

$$\rho_{2_-}(x) = -2e\int_{-\infty}^{\infty} n_-(E)f_-(E)\,dE$$

$$= -2e\int_{-\infty}^{v_2+e\Delta V_2} n_-(E)f_-(E)\,dE - 2e\int_{v_2+e\Delta V_2}^{\chi_2+e\Delta V_2} n_-(E)f_-(E)\,dE - 2e\int_{\chi_2+e\Delta V_2}^{\infty} n_-(E)f_-(E)\,dE\,,$$

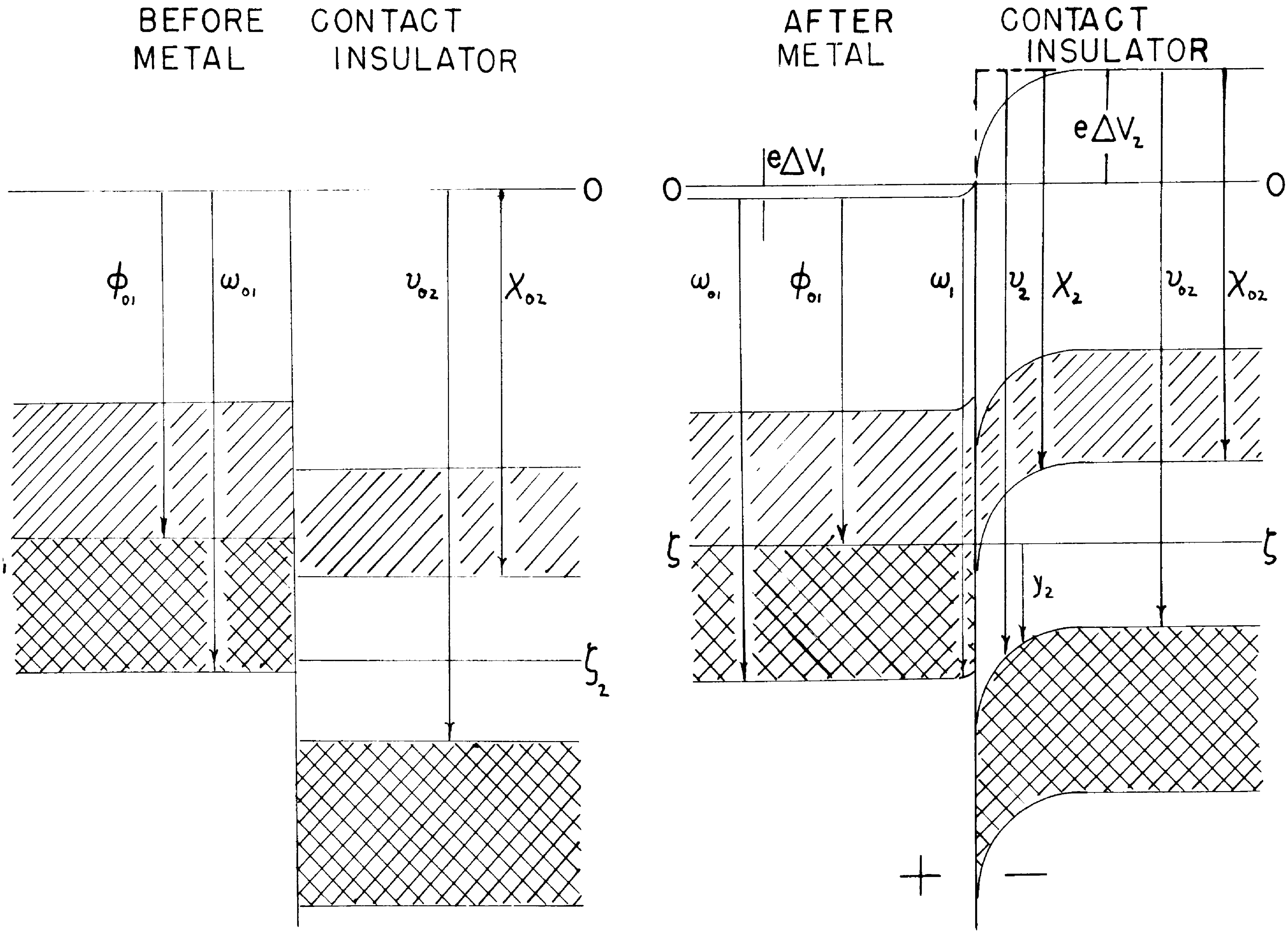

Figure 2. Schematic Energy-Band Diagram: Fermi Level of Metal above Fermi Level of Insulator, Top of Filled Band of Metal above Bottom of Empty Band of Insulator

while the positive charge density is given by

$$\rho_{2_+}(x) = 2e\int_{-\infty}^{\infty} n_+(E)\,f_+(E)\,dE$$

$$= 2e\int_{-\infty}^{\mathcal{V}_2+e\Delta V_2} n_+(E)\,f(E)\,dE + 2e\int_{\mathcal{V}_2+e\Delta V_2}^{\chi_2+e\Delta V_2} n_+(E)\,f_+(E)\,dE + 2e\int_{\chi_2+e\Delta V_2}^{\infty} n_+(E)\,f_+(E)\,dE\,.$$

In the range $\mathcal{V}_2+e\Delta V_2$ to $\chi_2+e\Delta V_2$ the energy level density is zero for electrons and positive charge. We have

$$f_+(E) = \begin{cases} 0 & \mathcal{V}_2+e\Delta V_2 < E < \infty \\ 1 & -\infty < E < \mathcal{V}_2+e\Delta V_2 \end{cases},$$

because every possible state for positive charge is occupied below $\mathcal{V}_2+e\Delta V_2$, and empty above $\mathcal{V}_2+e\Delta V_2$, this being based on the assumption that the nuclei stay fixed in the process of charge transfer.

The net total charge density becomes

$$\rho_2(x) = \rho_{2_-}(x)+\rho_{2_+}(x) = 2e\int_{-\infty}^{\mathcal{V}_2+e\Delta V_2}[1-f_-(E)]\,n_-(E)\,dE - 2e\int_{\chi_2+e\Delta V_2} f_-(E)\,n_-(E)\,dE\,,$$

where $$1 - f_-(E) = \frac{1}{e^{(\zeta-E)/kT}+1}\,.$$

The first integral, which pertains to the lower band, is concerned with a nearly-filled band, and the density of states has the inverted form. The second integral concerning excess electrons near the bottom of the upper band has the density function of standard form. Then we have

$$\rho_2(x) = 4\pi\left(\frac{2m_2^*}{h^2}\right)^{\frac{3}{2}} e\int_{-\infty}^{\mathcal{V}_2+e\Delta V_2}\frac{[\mathcal{V}_2+e\Delta V_2-E]^{\frac{1}{2}}}{e^{(\zeta-E)/kT}+1}\,dE - 4\pi\left(\frac{2m_2^*}{h^2}\right)^{\frac{3}{2}}\int_{\chi_2+e\Delta V_2}^{\infty}\frac{[E-(\chi_2+e\Delta V_2)]^{\frac{1}{2}}}{e^{(E-\zeta)/kT}+1}\,dE\,.$$

Changing variables in the first and second integrals to

$$kTx = v_2 + e\Delta V_2 - E \quad ; \quad kT\xi = -(\chi_2 + e\Delta V_2 - \zeta);$$

and $kTx = E - (\chi_2 + e\Delta V_2)$; $kT\xi = -(\chi_2 + e\Delta V_2 - \zeta)$,

respectively, where $\chi_2 + \sigma = v_2$ and $\gamma = \sigma/kT$,

we have

$$\rho_2(x) = 4\pi e\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{e^{x+\xi-\gamma}+1} - 4\pi e\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\int_0^\infty \frac{x^{\frac{1}{2}}\,dx}{e^{x-\xi}+1}.$$

Defining[12]

$$F_n(\xi) = \int_0^\infty \frac{x^n\,dx}{e^{x-\xi}+1},$$

we finally have

$$(1) \qquad \rho_2(x) = 4\pi e\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\},$$

if the effective masses of the electrons in the two bands are equal. This relation, together with Poisson's equation, will lead us to the potential variation in the insulator.

1. Solution of Poisson's Equation. We have

$$\frac{d^2V_2}{dx^2} = -\frac{4\pi}{\epsilon_2}\rho_2(x) = -\frac{16\pi^2 e}{\epsilon_2}\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\}.$$

Letting $v_2 = -eV_2$,

$$\frac{d^2v_2}{dx^2} = A_2\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\}, \quad \text{where } A_2 = \frac{16\pi^2 e^2}{\epsilon_2}\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}};$$

or

$$\frac{d}{dv_2}\left[\frac{1}{2}\left(\frac{dv_2}{dx}\right)^2\right] = A_2\left\{F_{\frac{1}{2}}[(\sigma+\chi_2+e\Delta V_2-\zeta)/kT] - F_{\frac{1}{2}}[-(\chi_2+e\Delta V_2-\zeta)/kT]\right\}.$$

Letting $y_2 = v_2 + e\Delta V_2 - \zeta = \chi_2 + e\Delta V_2 - \zeta$, and $u_2 = y_2/kT$,

we have

$$\frac{d}{du_2}\left[\frac{1}{2}\left(\frac{du_2}{dx}\right)^2\right] = \frac{A_2}{kT}\left\{F_{\frac{1}{2}}(u_2) - F_{\frac{1}{2}}(\gamma-u_2)\right\}.$$

Integrating, with the boundary condition that as $x \to \infty$ the field strength vanishes (by conservation of charge), we have

$$(2) \quad \left(\frac{du_2}{dx}\right)^2 = \frac{2A_2}{kT}\int_{u_{02}}^{u_2}\left\{F_{\frac{1}{2}}(u_2) - F_{\frac{1}{2}}(\gamma - u_2)\right\}du_2 ,$$

where

$$u_{02} = u_2 \quad at \quad x \to \infty .$$

Introducing the relation [12] $\frac{2}{3}F_{\frac{3}{2}}(\eta) = \int_a^\eta F_{\frac{1}{2}}(\eta)d\eta + \frac{2}{3}F_{\frac{3}{2}}(a)$,

and integration from o to x we see

$$\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}x = \int_{u_{02}-\frac{e\Delta V_2}{kT}}^{u_2}\frac{du_2'}{\left\{\frac{2}{3}F_{\frac{3}{2}}(u_2') - \frac{2}{3}F_{\frac{3}{2}}(u_{02}) - \frac{2}{3}F_{\frac{3}{2}}(\gamma - u_{02}) + \frac{2}{3}F_{\frac{3}{2}}(\gamma - u_2')\right\}^{\frac{1}{2}}},$$

where

$$u_2(x=0) = u_{02} - \frac{e\Delta V_2}{kT} \quad and \quad u_{02} - \frac{e\Delta V_2}{kT} \leq u_2' \leq u_{02} .$$

From Figure 2 we see that γ and u_{02} are negative and $e\Delta V_2/kT$ is positive, and that they are in the order $\gamma < u_{02} < e\Delta V_2/kT$. The function $F_{\frac{3}{2}}(u_2')$ increases rapidly for positive values of u_2', but is small for negative value of u_2'. If we stay sufficiently far from u_{02} we may retain only the last term in the denominator. We have then

$$(3) \quad \left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}x = \int_{u_{02}-\frac{e\Delta V_2}{kT}}^{u_2}\frac{du_2'}{\left\{\frac{2}{3}F_{\frac{3}{2}}(\gamma - u_2')\right\}^{\frac{1}{2}}}, \quad (x \geq 0)$$

where $u_2 \leq u_{02} - \varepsilon$, ε being a positive quantity. This gives us an intrinsic expression for the potential as a function of distance in the insulator.

From equation (5) of Chapter II we have the corresponding equation for the metal

$$(4) \quad x = l_1 \ln\left(\frac{\omega_1 - \omega_{01}}{-e\Delta V_1}\right), \qquad (x \leq 0)$$

where $e\Delta V_1$ is negative.

Equations (3) and (4) contain the unknowns $e\Delta V_1$ and $e\Delta V_2$. They are determined by the conditions that at the contact the field strength is continuous and that at infinity $\phi_{01} + e\Delta V_1 = \zeta$ and $v_{02} + e\Delta V_2 - y_{02} = \zeta$.

2. Evaluation of the Quantities $e\Delta V_1$, $e\Delta V_2$ and ζ.

From equation (3) we find that

$$(5) \quad \left.\frac{dv_2}{dx}\right|_{x=0} = (2A_2 kT)^{\frac{1}{2}}\left\{\frac{2}{3} F_{\frac{3}{2}}\left[(\sigma - y_{02} + e\Delta V_2)/kT\right]\right\}^{\frac{1}{2}},$$

where we have taken the positive sign since the slope is everywhere positive; and from (4)

$$(6) \quad \left.\frac{d\omega_1}{dx}\right|_{x=0} = \frac{-e\Delta V_1}{l_1}.$$

From our conditions at infinity

$$(7) \quad \phi_{01} + e\Delta V_1 = \zeta,$$

$$(8) \quad \text{and} \quad v_{02} + e\Delta V_2 - y_{02} = \zeta;$$

$$\text{so} \quad \phi_{01} + e\Delta V_1 = v_{02} + e\Delta V_2 - y_{02},$$

$$(9) \quad \text{or} \quad e\Delta V_2 - e\Delta V_1 = \phi_{01} - v_{02} + y_{02}.$$

Assuming ζ to lie half way between the bands, we have $\sigma = 2y_{02}$. Then (5) becomes

$$(10)\qquad \left.\frac{dV_2}{dx}\right|_{x=0} = (2A_2kT)^{\frac{1}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}\left[\left(\frac{\sigma}{2}+e\Delta V_2\right)/kT\right]\right\}^{\frac{1}{2}}$$

Substituting (9) into (6) we find

$$(11)\qquad \left.\frac{d\omega_1}{dx}\right|_{x=0} = \frac{\phi_{01}-\chi_{02}-\frac{1}{2}\sigma-e\Delta V_2}{l_1}.$$

Equating (10) and (11), we get

$$\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}\left[\left(\frac{\sigma}{2}+e\Delta V_2\right)/kT\right]\right\}^{\frac{1}{2}} = \frac{\left(\phi_{01}-\chi_{02}-\frac{1}{2}\sigma-e\Delta V_2\right)/kT}{l_1}.$$

If $\eta \equiv \left(\frac{\sigma}{2}+e\Delta V_2\right)/kT$ and $\beta \equiv \left(\phi_{01}-\chi_{02}\right)/kT$ (>0),

then $$\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}(\eta)\right\}^{\frac{1}{2}} = \frac{\beta-\eta}{l_1}.$$

(12) or $$\left\{\frac{2}{3}F_{\frac{3}{2}}(\eta)\right\}^{\frac{1}{2}} = A - B\eta,$$ where $$A = \frac{\beta}{\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}l_1}$$ and $$B = \frac{1}{\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}l_1}.$$

This equation may be solved graphically for η, and hence $e\Delta V_2$. We take for m_2^* the normal mass of the electron, and set $\epsilon_2 = \epsilon_1 = 1$, and T = 300° K. A value of $y_{01} = 3.19$ e.v. is assumed for half the band width (as would be the value for sodium). This gives $l_1 = .673 \times 10^{-8}$ cm and

$$\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}} = 6.26 \times 10^{7}\ \text{cm}^{-1},$$

whence B = 2.38 and A = 2.38β.

For a specific example,

$$\chi_{02} = -7\,\text{e.v.}\qquad \phi_{01} = -6.27\,\text{e.v.}\qquad \mathcal{V}_{02} = -10\,\text{e.v.}$$

so $\beta = 292$

and $A = 69.5$.

Figure 3 shows a plot of (12). We see that the two curves intersectat at $\eta = 20$, $y = 22$;

so $$\left(\frac{\mathcal{V}_{02} - \chi_{02}}{2} + e\Delta V_2 \right) \Big/ kT = 20,$$

and $e\Delta V_2 = 2$ e.v..

From (8), $\zeta = \mathcal{V}_{02} + e\Delta V_2 - y_{02}$. The gap between the valence and conduction band of the insulator is $\sigma = -3$ ev, so

$$y_{02} = \frac{\sigma}{2} = -1.5 \text{ e.V}$$

and $\zeta = -6.5$ e.v..

From (7) $e\Delta V_1 = \zeta - \phi_{01} = -0.23$ e.v..

Knowing the shift in potential and the position of the Fermi level at equilibrium, we are ready to calculate the surface and volume charge density in the insulator.

<u>3. Calculation of the Surface Charge Density.</u> By application of Gauss' law to a plane conductor carrying a surface charge σ_2, the electric field outside is given by

$E = 2\pi\sigma_2$.

Since $E = -\dfrac{\partial V_2}{\partial x}$,

$$\sigma_2 = -\frac{1}{2\pi} \frac{\partial V_2}{\partial x} = \frac{kT}{2\pi e} \frac{du_2}{dx},$$

where $\dfrac{du_2}{dx}$ is a function of u_2 as seen from equation (2).

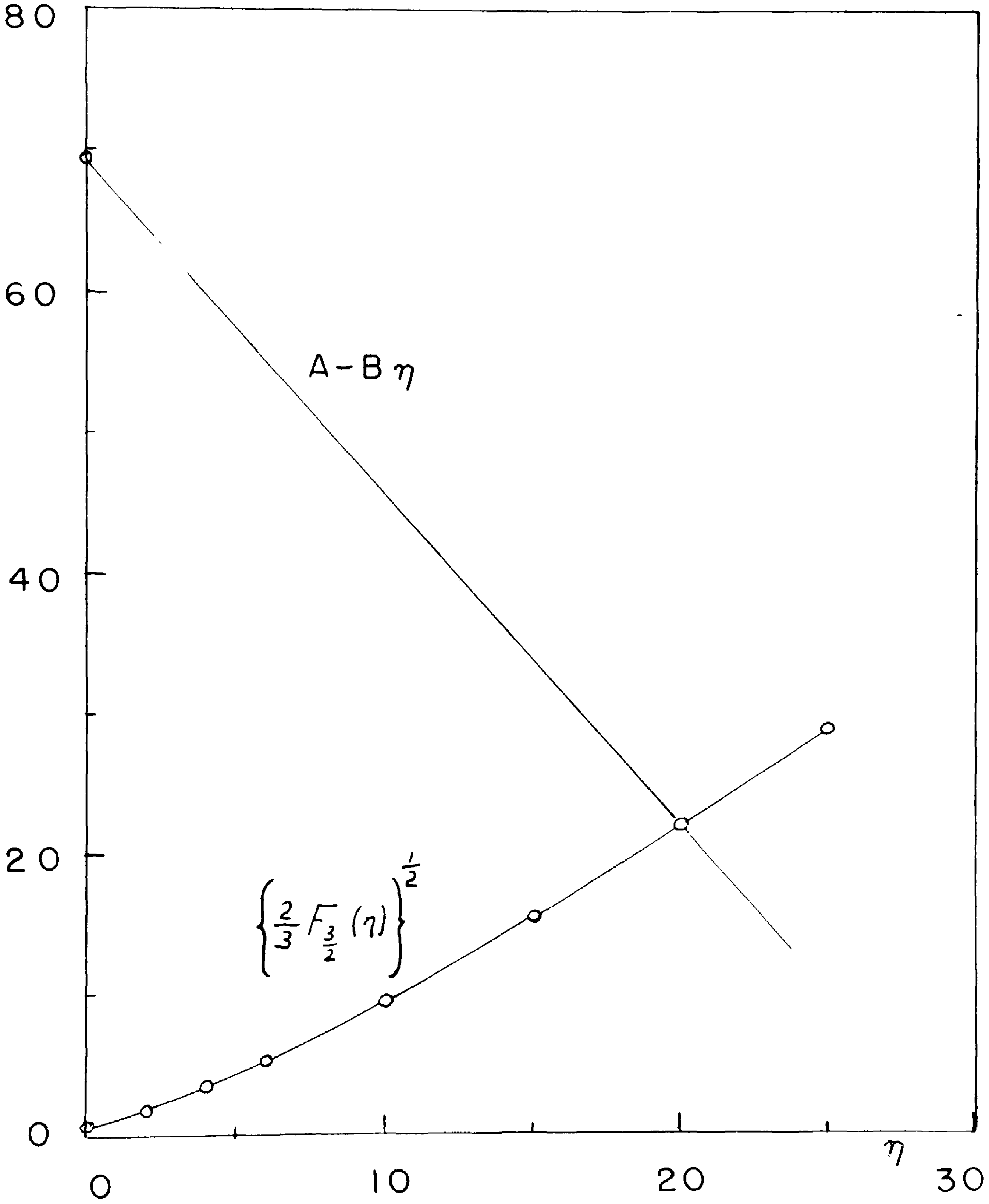

Figure 3. Graph for Solution of Equation 12, Section B 2, Chapter IV

The expression may be simplified as in equation (3) by defining $\mathcal{X} \equiv \gamma - u_2$, to give

$$\frac{du_2}{dx} = \left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}(\mathcal{X})\right\}^{\frac{1}{2}} .$$

We have then

$$\sigma_2(\mathcal{X}) = \left(\frac{kT}{2\pi e}\right)\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}(\mathcal{X})\right\}^{\frac{1}{2}},$$

where x is determined for corresponding values of $u_2 \equiv \gamma - \mathcal{X}$ by equation (3). It should be noted that σ_2(o) is an effective "surface charge" density in the sense that it is a measure of the charge to the right of the contact.

The following table shows the results:

TABLE I

$\mathcal{X}$	x (Å)	$\sigma_2(\mathcal{X})$ (esu)	$100\ \sigma_2(\mathcal{X})/\sigma_2(20)$
20	0	18300	100%
8	1.5	6050	33
0	7	720	3.9
-4	26	105	.57
-20	76,000	.035	.00019

We see that about 70% of the charge is located within 1-1/2 angstroms from the interface.

4. Calculation of the Volume Charge Density. From equation (1) we have

$$\rho_2(x) = \frac{A_2}{4\pi e}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\} .$$

For values of say $\xi > -30$ we may approximate this expression by

$$\rho_2(x) = -\frac{A_2}{4\pi e}\left\{F_{\frac{1}{2}}(\xi)\right\}.$$

The following table shows the results:

TABLE II

ξ	$x(\text{Å})$	$\rho_2(x)(esu)$	$100\,\rho_2(x)/\rho_2(0)$
20	0	770×10^9	100%
0	7	8.8×10^9	1.1
-4	26	0.21×10^9	.027

C. Case of Large Charge Transfer from Insulator to Metal

An analysis for Figure 4 similar to that for Figure 3 shows that the volume charge density in the insulator is

(1) $$\rho_2(\xi) = 4\pi e\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\},$$

except that now $e\Delta V_1$ is positive and $e\Delta V_2$ negative. We solve for the potential energy variation $\chi_2 = -eV_2$ by means of Poisson's equation:

$$\frac{d\chi_2}{dx^2} = A_2\left\{F_{\frac{1}{2}}\left[(\sigma+\chi_2+e\Delta V_2-\zeta)/kT\right] - F_{\frac{1}{2}}\left[-(\chi_2+e\Delta V_2-\zeta)/kT\right]\right\},$$

where $kT\xi \equiv -(\chi_2 + e\Delta V_2 - \zeta)$.

Letting $z_2 = \chi_2 + e\Delta V_2 - \zeta$ and $g_2 = z_2/kT$,

$$\frac{d}{dg_2}\left[\frac{1}{2}\left(\frac{dg_2}{dx}\right)^2\right] = \frac{A_2}{kT}\left\{F_{\frac{1}{2}}(\gamma+g_2) - F_{\frac{1}{2}}(-g_2)\right\}.$$

Integrating with the boundary conditions that as $x \rightarrow \infty$ the field strength vanishes, we have

$$(2) \quad \left(\frac{dq_2}{dx}\right)^2 = \frac{2A_2}{kT}\int_{q_{02}}^{q_2}\left\{F_{\frac{1}{2}}(\gamma+q_2') - F_{\frac{1}{2}}(-q_2')\right\}dq_2' \, .$$

Introducing the relation[12] $\frac{2}{3}F_{\frac{3}{2}}(\eta) = \int_0^{\eta} F_{\frac{1}{2}}(\eta)\,d\eta + \frac{2}{3}F_{\frac{3}{2}}(a)$,

and integrating from o to x we see

$$-\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}} x = \int_{q_{02}-e\Delta V_2/kT}^{q_2} \frac{dq_2'}{\left\{\frac{2}{3}F_{\frac{3}{2}}(\gamma+q_2') - \frac{2}{3}F_{\frac{3}{2}}(\gamma+q_{02}) - \frac{2}{3}F_{\frac{3}{2}}(-q_{02}) + \frac{2}{3}F_{\frac{3}{2}}(-q_2')\right\}^{\frac{1}{2}}} \, .$$

where

$$q_{02} - \frac{e\Delta V_2}{kT} \geqslant q_2' \geqslant q_{02} \, .$$

Here the positive root is extraneous, and we discard it. If we restrict the upper limit to $q_2 \leq q_{02} + \varepsilon$ where $\varepsilon > 0$ and is sufficiently large, we may retain only the first term giving

$$(3) \quad -\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}} x = \int_{q_{02}-\frac{e\Delta V_2}{kT}}^{q_2} \frac{dq_2'}{\left\{\frac{2}{3}F_{\frac{3}{2}}(\gamma+q_2')\right\}^{\frac{1}{2}}} \, .$$

We now have an expression for the potential versus distance in the insulator.

From Chapter III equation (5) we have the corresponding equation for the metal

(4) $x = l_1 \ln\left(\frac{\omega_1 - \omega_{01}}{-e\Delta V_1}\right)$ $(x \leq 0)$ where now $e\Delta V_1$ is positive.

We solve for $e\Delta V_1$ and $e\Delta V_2$ in equation (3) and (4) by the condition that at the boundary the field strength must be

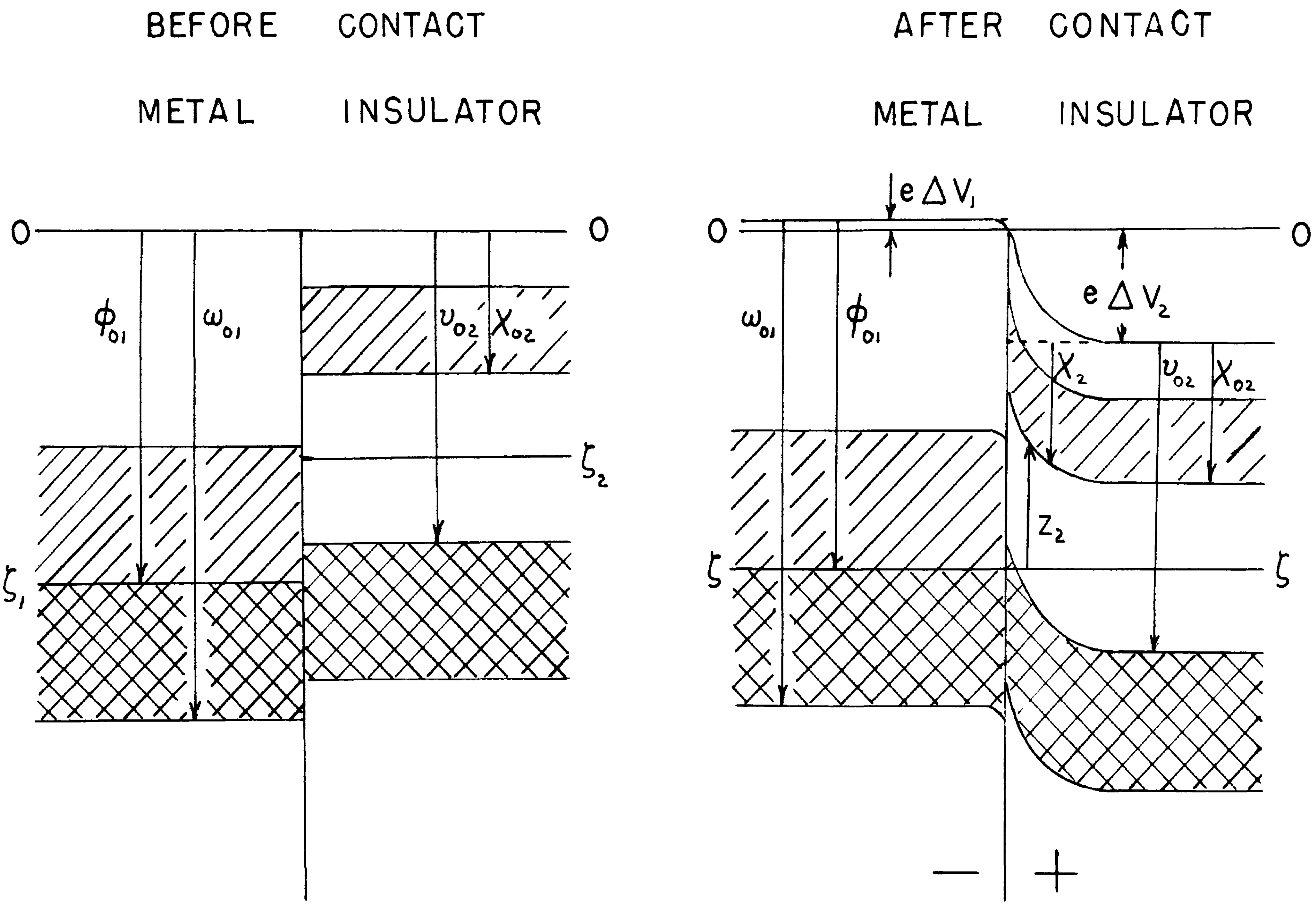

Figure 4. Schematic Energy-Band Diagram: Fermi Level of Metal below Fermi Level of Insulator, Top of Filled Band of Insulator above Top of Filled Band of Metal

continuous and that at infinity

$$(5) \quad \phi_{01} + e\Delta V_1 = \zeta \quad \text{and} \quad \chi_{02} + e\Delta V_2 - z_{02} = \zeta .$$

1. Evaluation of the Quantities $e\Delta V_1$, $e\Delta V_2$ and ζ.

From equation (2)

$$(6) \quad \left.\frac{d\chi_2}{dx}\right|_{x=0} = -(2A_2 kT)^{\frac{3}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}\left[(\sigma + z_{02} - e\Delta V_2)/kT\right]\right\}^{\frac{1}{2}},$$

and from (4)

$$(7) \quad \left.\frac{d\omega_1}{dx}\right|_{x=0} = \left(\phi_{01} - V_{02} + \frac{\sigma}{2} - e\Delta V_2\right)/\ell_1$$

Eliminating ζ from (5) gives $e(\Delta V_2 - \Delta V_1) = \phi_{01} - \chi_{02} + z_{02}$.

Continuity of field strength requires that (6) and (7) be equal:

$$-\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\left\{\frac{2}{3}F_{\frac{3}{2}}\left[\left(\frac{\sigma}{2} - e\Delta V_2\right)/kT\right]\right\}^{\frac{1}{2}} = \left(\phi_{01} - V_{02} + \frac{\sigma}{2} - e\Delta V_2\right)/\ell_1 kT .$$

Placing $\eta^{*} \equiv \left(\frac{\sigma}{2} - e\Delta V_2\right)/kT$ and $\beta^{*} \equiv (\phi_{01} - V_{02})/kT \quad (<0)$

gives

$$(8) \quad -\left\{\frac{2}{3}F_{\frac{3}{2}}(\eta^{*})\right\}^{\frac{1}{2}} = A^{*} + B^{*}\eta^{*},$$

where $A^{*} = \beta^{*}/\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\ell_1$, $B^{*} = 1/\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\ell_1$.

Equation (8) may be solved graphically for $e\Delta V_2$. Taking m_2 to be the normal mass of the electron, $\varepsilon_1 = \varepsilon_2 = 1$, $T = 300^\circ$ K, and $y_{01} = 3.19$ e.V., we get

$$\ell_1 = 673 \times 10^{-8}\ \text{cm} \quad \text{and} \quad \left(\frac{2A_2}{kT}\right)^{\frac{1}{2}} = 6.26 \times 10^{7}\ \text{cm}^{-1} .$$

Therefore $B^* = 2.38$ and $A^* = 2.38$.

For a specific example

$$\chi_{02} = -2.54 \text{ e.v.}, \quad V_{02} = -5.54 \text{ e.v.}, \quad \phi_{01} = -6.27 \text{ e.v.},$$

$$\beta^* = -29.2,$$

and $A = -69.5$.

We are to plot therefore $\left\{\frac{2}{3} F_{\frac{1}{2}}(\eta^*)\right\}^{\frac{1}{2}} = -\left[-69.5 + 2.38\eta^*\right]$, just as in Figure 3. The curves are found to intersect at at $\eta^* = 20$, $y = 22$.

Now $$\left(\frac{V_{02} - \chi_{02}}{2} - e\Delta V_2\right)\Big/kT = 20 ;$$

therefore, $e\Delta V_2 = -2 \text{ e.v.},$

and assuming $\sigma = -3 \text{ e.v.}, \qquad z_2 = -\frac{\sigma}{2} = 1.5 \text{ e.v.},$

$$\zeta = \chi_{02} + e\Delta V_2 - z_{02} = -6.04 \text{ e.v.}.$$

Finally,

$$e\Delta V_1 = \zeta - \phi_{01} = .23 \text{ e.v.}.$$

Knowing the shift of potential and the position of the Fermi level at equilibrium, we are ready to calculate the surface and volume charge density in the insulator.

2. Calculation of the Surface and Volume Charge Density. As in part 3 of Section B we have for the surface charge density $\sigma_2(t) = \frac{kT}{2\pi e}\left(\frac{2A_2}{kT}\right)^{\frac{1}{2}}\left\{\frac{2}{3} F_{\frac{3}{2}}(t)\right\}^{\frac{1}{2}}$, with $t \equiv \gamma + q_2$.

The variable t has the same values here as in part 3 of Section B since $q_2 = -a_2$; therefore, the results are identical to those in Table I on page 28 except the charge has the opposite sign.

The volume charge density has the form

$$\rho_2(x) = \frac{A_2}{4\pi e}\left\{F_{\frac{1}{2}}(\gamma-\xi)-F_{\frac{1}{2}}(\xi)\right\}.$$

which is also identical with the result of part 4 of Section B. Table II, in the same section is applicable with the charge of opposite sign.

D. The Case of Small Charge Transfer from Metal to Insulator

In this example, Figure 5, electrons escape by thermal agitation from the filled band in the metal to the empty band of the insulator. A small amount of charge is lost by the metal in a small spatial region, and the same amount is gained by the insulator in a large spatial region.

Applying Fermi-Dirac statistics to the energy band structure we again arrive at the expression

(1) $$\rho_2(x) = 4\pi e\left(\frac{2m_2^*kT}{h^2}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\}$$

for the volume charge density. Letting $\chi_2 = -eV$ we have for Poisson's equation

$$\frac{d^2\chi_2}{dx^2} = A_2\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\} \qquad \text{with } A_2 = \frac{16\pi^2e^2}{\epsilon_2}\left(\frac{2m_2^*kT}{h^2}\right)^{\frac{3}{2}},$$

and $\xi = -(\chi_2 + e\Delta V_2 - \zeta)/kT$.

For a specific case let us take

$$\chi_{02} = -6\text{ e.V.} \qquad V_{01} = -11\text{ e.V.} \qquad \phi_{01} = -6.27\text{ e.V.} \qquad \epsilon_2 = 1 \ .$$

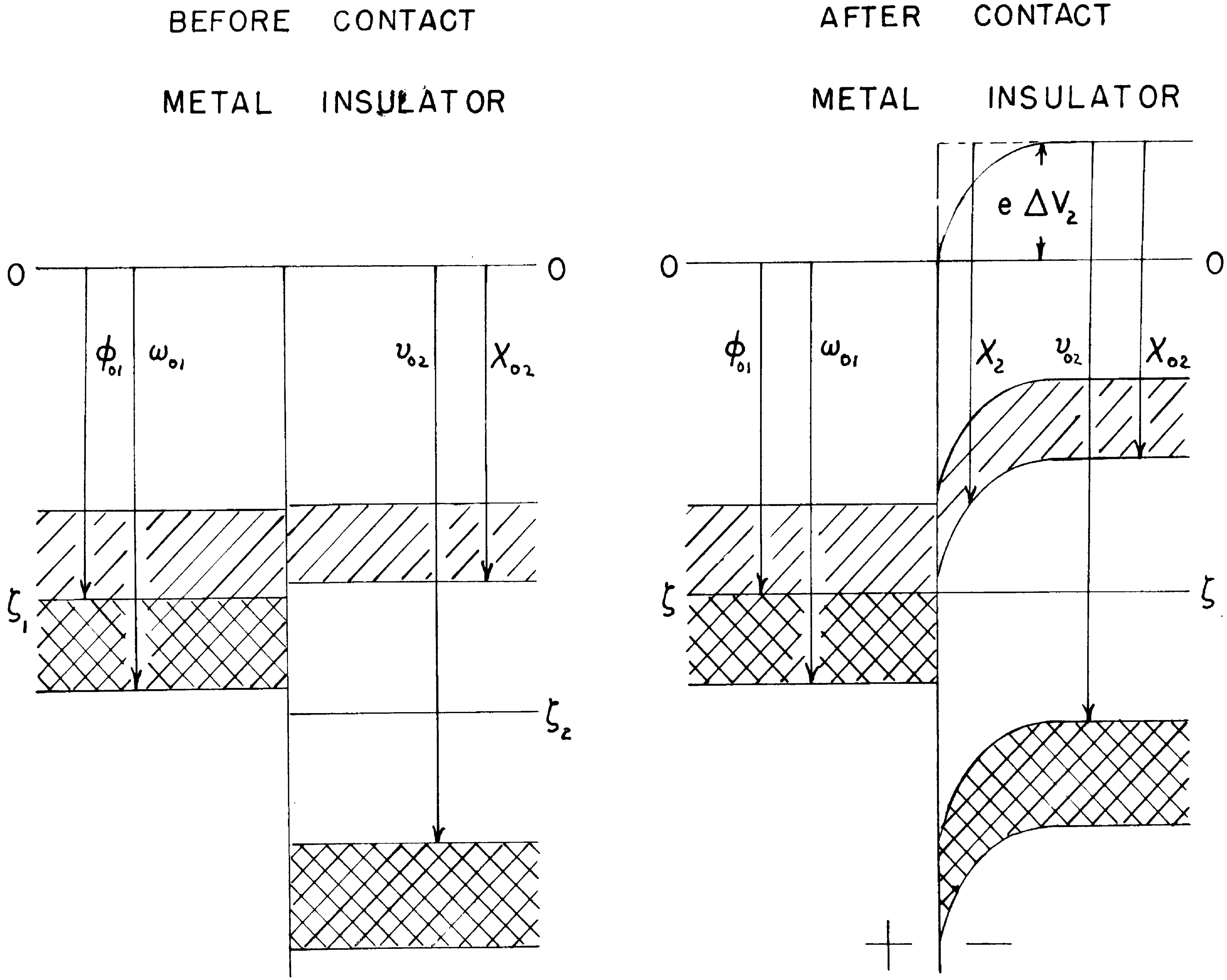

Figure 5. Schematic Energy-Band Diagram: Fermi Level of Metal above Fermi Level of Insulator, Top of Filled Band of Metal below Empty Band of Insulator

We see from the figure that ζ and γ are negative quantities with $\gamma < \zeta$ for all x, and so we may neglect the first term in the expression for the charge density provided we are not too far from the contact, giving for Poisson's equation

$$\frac{d^2\chi_2}{dx^2} = -A_2 F_{\frac{1}{2}}(\zeta) .$$

Since ζ is negative we may also use the series representation[12] for $F_{\frac{1}{2}}(\zeta)$ and obtain

$$\frac{d^2\chi_2}{dx^2} = -A_2 \Gamma(\tfrac{3}{2}) \sum_{s=1}^{\infty} (-1)^{s-1} \frac{e^{s\zeta}}{s^{3/2}} .$$

If ζ is sufficiently large and negative, we may approximate the series by retaining only the first term. The error is about 0.6% if $\zeta = -4$, and negligibly small for $\zeta = -20$, the greatest value of ζ occurring in our example.

We finally have

$$\frac{d^2\chi_2}{dx^2} = -B_2 e^{\zeta} \qquad \text{where} \quad B_2 = A_2 \Gamma(\tfrac{3}{2}) .$$

Solving in the usual manner subject to the condition that at infinity the field strength vanishes, we find

(2) $$\chi_2 = kT \ln\left[\left(\frac{C_2}{2}\right)^{\frac{1}{2}} x + D_2 \right]^2 \qquad (x \geq 0) ,$$

where $C_2 = \dfrac{B_2}{kT} e^{-(e\Delta V_2 - \zeta)/kT}$ and $D_2 = e^{\frac{1}{2}(\chi_{02} - e\Delta V_2)/kT}$.

(3) For the metal we have $\omega_1 - \omega_{01} = -e\Delta V_1 e^{x/\ell_1} \qquad (x \leq 0)$ where $e\Delta V_1$ is negative.

We make use of the boundary conditions at the contact as before in order to solve for the unknowns $e\Delta V_1$, and $e\Delta V_2$.

It can be shown that $e\Delta V_1$ is negligible compared with $e\Delta V_2$. We can then take $\zeta \simeq \phi_{01}$ and $e\Delta V_2 = \zeta - \chi_{02} - \frac{\sigma}{2} = 2.23\,\text{e.v.}$

The surface charge density is computed in the usual manner:

$$(4) \quad \sigma_2(x) = \frac{kT}{2\pi e}\sqrt{2C_2}\, e^{-\chi_2/2kT} = 7.8 \times 10^2\, e^{-(e\Delta V_2 - \zeta)/2kT - \chi_2/2kT},$$

with $x = 0$, $\chi_2(0) = \chi_{02} - e\Delta V_2 = -8.23\,\text{e.v.}$

$$\sigma_2(0) = 3.52\ \text{statcoulombs}/\text{cm}^2.$$

The volume charge density is

$$(5) \quad \rho_2(x) = -4\pi e\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\Gamma\left(\tfrac{3}{2}\right)e^{\zeta} = -2e\left(\frac{2m_2^*\pi kT}{h^2}\right)^{3/2} e^{\zeta}$$

$$= -2.4 \times 10^{19}\, e\; e^{-(\chi_2 + e\Delta V_2 - \zeta)/kT},$$

and $\rho_2(0) = -2.35 \times 10^5\ \text{statcoulombs}/\text{cm}^3$.

It can be seen that the charge density falls to 1/4 of its value at the contact in 750Å. In cases where $\zeta - \chi_2$ differ by say 0.5 to 1 e.v. this distance ranges from about 10^6 to 10^{10} angstrom units, a value much greater than obtained in the previous two cases.

E. The Case of Small Charge Transfer from Insulator to Metal

Figure 6 represents an example where electrons escape from the insulator only by thermal agitation from the filled band in the insulator to the half-filled band in the metal. A small charge is lost by the insulator from a large spatial region and an equal charge is gained by the metal within a small spatial region.

Upon application of Fermi-Dirac statistics to the energy band structure, we have for the volume charge density again

$$(1) \qquad \rho_2(x) = 4\pi e \left(\frac{2m^* kT}{h^2}\right)^{\frac{3}{2}} \left\{ F_{\frac{1}{2}}(\gamma-\zeta) - F_{\frac{1}{2}}(\zeta) \right\}.$$

Poisson's equation becomes

$$\frac{d^2 v_2}{dx^2} = A_2 \left\{ F_{\frac{1}{2}}(\gamma-\zeta) - F_{\frac{1}{2}}(\zeta) \right\},$$

where $v_2 = -eV$, $\zeta = -(\chi_2 + e\Delta V_2 - \zeta)/kT$ and $A_2 = \frac{16\pi^2 e^2}{\varepsilon_2}\left(\frac{2m_2^* kT}{h^2}\right)^{3/2}$.

We solve in the same manner as Section D, except that we neglect the second term in (1) compared with the first, obtaining

$$(2) \qquad v_2 = -kT \ln\left[D_2 + \left(\frac{C_2}{2}\right)^{\frac{1}{2}} x\right]^2, \qquad (x \geq 0)$$

with $D_2 = e^{\frac{1}{2}(-v_{02} + e\Delta V_2)/kT}$,

$C_2 = \mathcal{B}_2 \, e^{(\Delta V_2 - \zeta)/kT}_{/kT}$, and $\mathcal{B}_2 = \Gamma(\frac{3}{2}) A_2$.

For the metal we have $\omega_1 - \omega_{01} = -e\Delta V_1 e^{x/\delta_1}$, $(x \leq 0)$ where $e\Delta V_1$ is positive.

Making use of the boundary conditions as before, we solve for $e\Delta V_1$ and $e\Delta V_2$. As in Section D, $e\Delta V_1$ is negligible compared with $e\Delta V_2$, and so $\zeta \approx \phi_{01}$. As a specific example, take $v_{02} = -7$ e.v. $\chi_{02} = -3$ e.v. $\phi_{01} = -6$ e.v.

then $e\Delta V_2 = \zeta - v_{02} + \frac{\sigma}{2} = -1$ e.v..

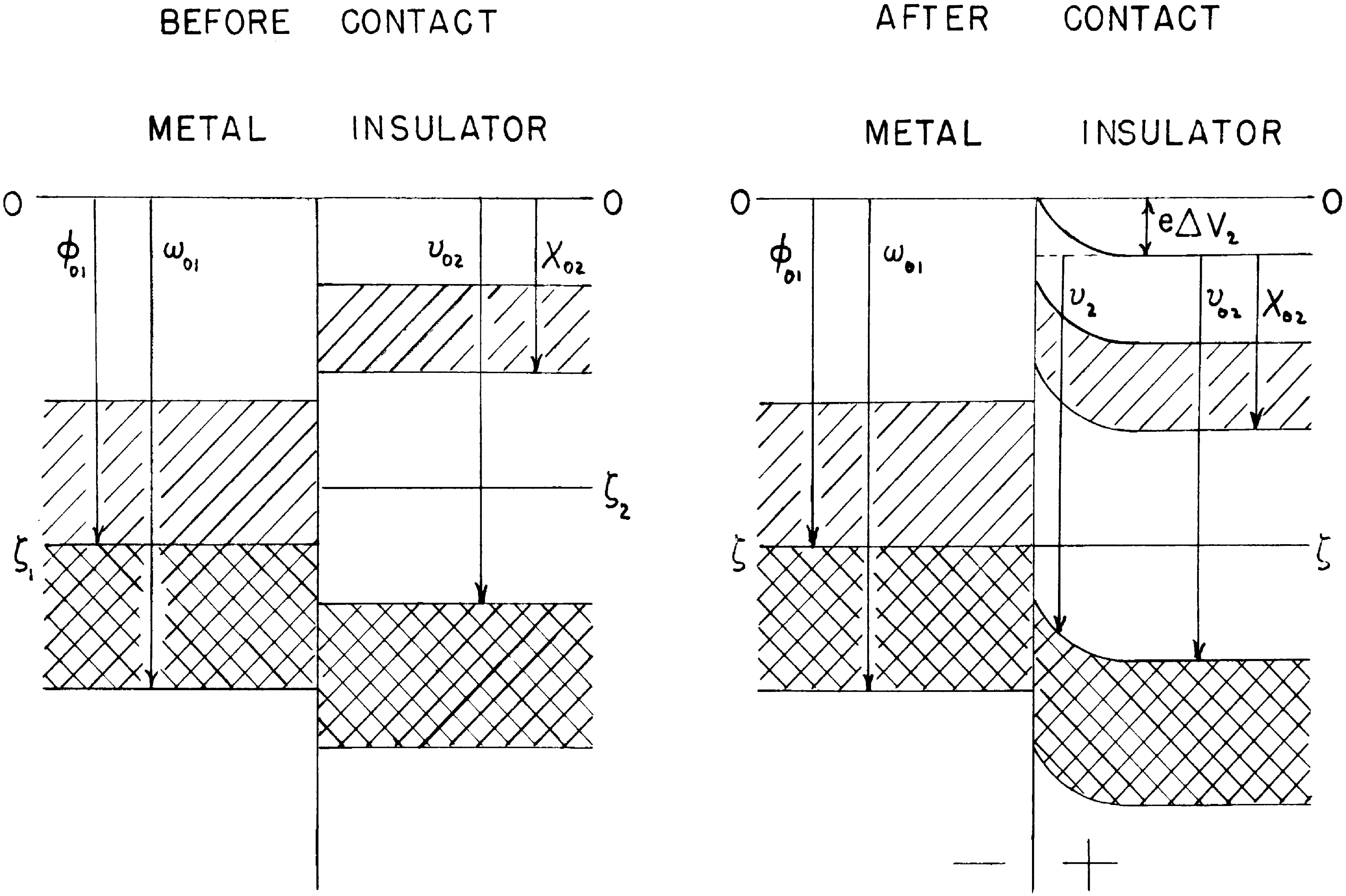

Figure 6. Schematic Energy-Band Diagram: Fermi Level of Metal below Fermi Level of Insulator, Top of Filled Band of Metal below Bottom of Empty Band of Insulator

The surface and volume charge densities follow the same form as those of Section D with the exception that the charge is of opposite sign. It is, therefore, not worthwhile to discuss this case further here.

CHAPTER V

INSULATOR-INSULATOR CONTACTS

A. General Behavior

In this chapter we discuss two cases of insulator-insulator contacts. The energy band structure is represented in Figures 7 and 8. Figure 7 illustrates conditions where electrons can escape from the left-hand insulator to the right-hand one only by thermal agitation from a filled band into an empty band at higher energy. Hence, small charge (perhaps 10^{-1} statcoulombs /cm^2) is lost by the left-hand insulator from a large spatial region (perhaps 10^6 A°) and an equal charge gained by the right-hand insulator within a large spatial region. Figure 8 is the case where electrons can spill from the filled band of the left-hand material into the empty band of the right-hand material. Large charge, say 10^4 statcoulombs /cm^2, is lost by the left-hand insulator from a small spatial region, say 10 A°, and equal and opposite charge is gained by the right-hand material in a small spatial region. The following calculations give the quantitative data of the previous arguments.

B. Case of Small Charge Transfer

The insulator on the right has a band structure identical with that of the insulator in Figure 5.

We have, therefore, a volume charge density

$$(1) \qquad \rho_2(x) = 4\pi e \left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}} \left\{ F_{\frac{1}{2}}(\gamma - \zeta) - F_{\frac{1}{2}}(\zeta) \right\} .$$

The solution of Poisson's equation is

$$(2) \qquad \chi_2(x) = 2kT \ln\left[\left(\frac{C_2}{2}\right)^{\frac{1}{2}} x + D_2\right] . \qquad (x \geq 0)$$

where $D_2 = e^{\frac{1}{2}(\chi_{02} - e\Delta V_2)/kT}$, $C_2 = \frac{B_2}{kT} e^{-(e\Delta V_2 - \zeta)/kT}$

and $B_2 = A_2 \Gamma(\frac{3}{2})$.

The insulator on the left has a band structure similar to that of the insulator in Figure 6. The volume charge density is

$$(3) \qquad \rho_1(x) = 4\pi e \left(\frac{2m_1^* kT}{h^2}\right)^{\frac{3}{2}} \left\{ F_{\frac{1}{2}}(\gamma - \zeta) - F_{\frac{1}{2}}(\zeta) \right\} ,$$

and the solution of Poisson's equation is

$$(4) \qquad \mathcal{V}_1(x) = -2kT \ln\left[-\left(\frac{C_1}{2}\right)^{\frac{1}{2}} x + D_1\right] , \qquad (x \leq 0)$$

where $D_1 = e^{-\frac{1}{2}(\mathcal{V}_{01} - e\Delta V_1)/kT}$, $C_1 = \frac{B_1}{kT} e^{(e\Delta V_1 - \zeta)/kT}$,

and $B_1 = A_1 \Gamma(\frac{3}{2})$.

After equilibrium has been reached we see from Figure 7 that at infinity

$$(5) \qquad \mathcal{V}_{02} + e\Delta V_2 - \frac{\sigma_2}{2} = \zeta$$

$$(6) \qquad \text{and} \quad \mathcal{V}_{01} + e\Delta V_1 - \frac{\sigma}{2} = \zeta .$$

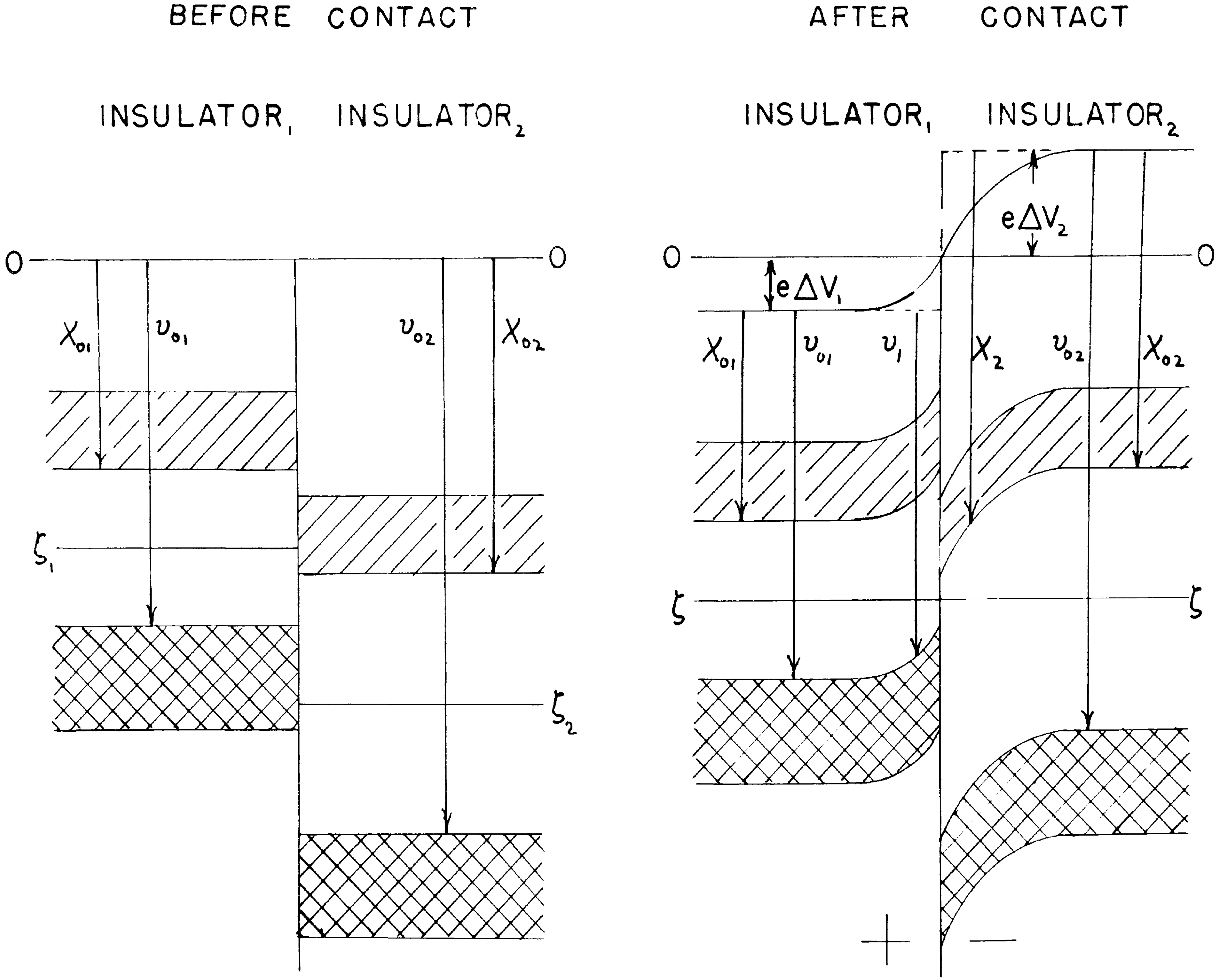

Figure 7. Schematic Energy-Band Diagram: Fermi Level of Insulator 1 above Fermi Level of Insulator 2, Filled Band of Insulator 1 below Empty Band of Insulator 2

These equations along with the condition at the boundary that the field strength must be continuous determine the unknowns $e\Delta V_1$ and $e\Delta V_2$.

From (2) and (3) respectively

$$\left.\frac{d\chi_2}{dx}\right|_{x=0} = \frac{2kT}{D_2}\left(\frac{C_2}{2}\right)^{\frac{1}{2}} ,$$

and

$$\left.\frac{dv_1}{dx}\right|_{x=0} = \frac{2kT}{D_1}\left(\frac{C_1}{2}\right)^{\frac{1}{2}} .$$

The continuity of field strength requires

$$\frac{C_1^{\frac{1}{2}}}{D_1} = \frac{C_2^{\frac{1}{2}}}{D_2} .$$

Inserting values for the C's and D's, and assuming the effective mass of electrons in the two insulators to be the same, we find that

$$(7) \qquad \zeta = \frac{1}{2}\left(v_{01} + \chi_{02}\right) .$$

From (6) and (7)

$$e\Delta V_1 = \frac{1}{2}\left(\chi_{02} - \chi_{01}\right) ,$$

and from (5) and (7)

$$e\Delta V_2 = \frac{1}{2}\left(v_{01} - v_{02}\right) .$$

For a specific case let us take $v_{01} = -7$, $\chi_{01} = -4$, $v_{02} = -11$ and $\chi_{02} = -6$ e.v.. This gives $\zeta = -6.5$ e.v. , $e\Delta V_1 = -1$ e.v. and $e\Delta V_2 = 2$ e.v. .

The expressions for the surface and volume charge densities in the right-hand insulator are identical with those in Section D, Chapter IV. We have, therefore, a charge density and depth of penetration which behave in exactly the same manner. The left-hand insulator has the same form as the insulator in Section E, Chapter IV, and, therefore, the charge density and depth of penetration are similar to those found in that section.

C. Case of Large Charge Transfer

In Figure 8 the right-hand insulator has a band structure the same as that of the insulator in Figure 2. Therefore, as developed in part 1 of Section B of Chapter IV, the charge density is

$$(1)\qquad \rho_2(x) = 4\pi e\left(\frac{2m_2^* kT}{h^2}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\},$$

and the solution of Poisson's equation is

$$(2)\qquad \left(\frac{2A_2}{kT}\right)^{\frac{1}{2}} x = \int_{u_{02}-e\Delta V_2/kT}^{u_2} \frac{du_2'}{\left\{\frac{2}{3}F_{\frac{3}{2}}(\gamma-u_2')\right\}^{\frac{1}{2}}} \qquad (x \geq 0)$$

The insulator on the left has a band structure the same as that of Figure 4. Therefore, as derived in Section C of Chapter IV, the volume charge density is

$$(3)\qquad \rho_1(x) = 4\pi e\left(\frac{2m_1^* kT}{h^2}\right)^{\frac{3}{2}}\left\{F_{\frac{1}{2}}(\gamma-\xi) - F_{\frac{1}{2}}(\xi)\right\},$$

and the solution of Poisson's equation is

$$(4)\qquad -\left(\frac{2A_1}{kT}\right)^{\frac{1}{2}} x = \int_{q_{01}-e\Delta V_1/kT}^{q_1} \frac{dq_1'}{\left\{\frac{2}{3}F_{\frac{3}{2}}(\gamma+q_1')\right\}^{\frac{1}{2}}} \qquad (x \leq 0)$$

After equilibrium has been reached it is seen from Figure 8 that an infinity

$$(5)\qquad \chi_{01} + e\Delta V_1 - z_{01} = \zeta_1 .$$

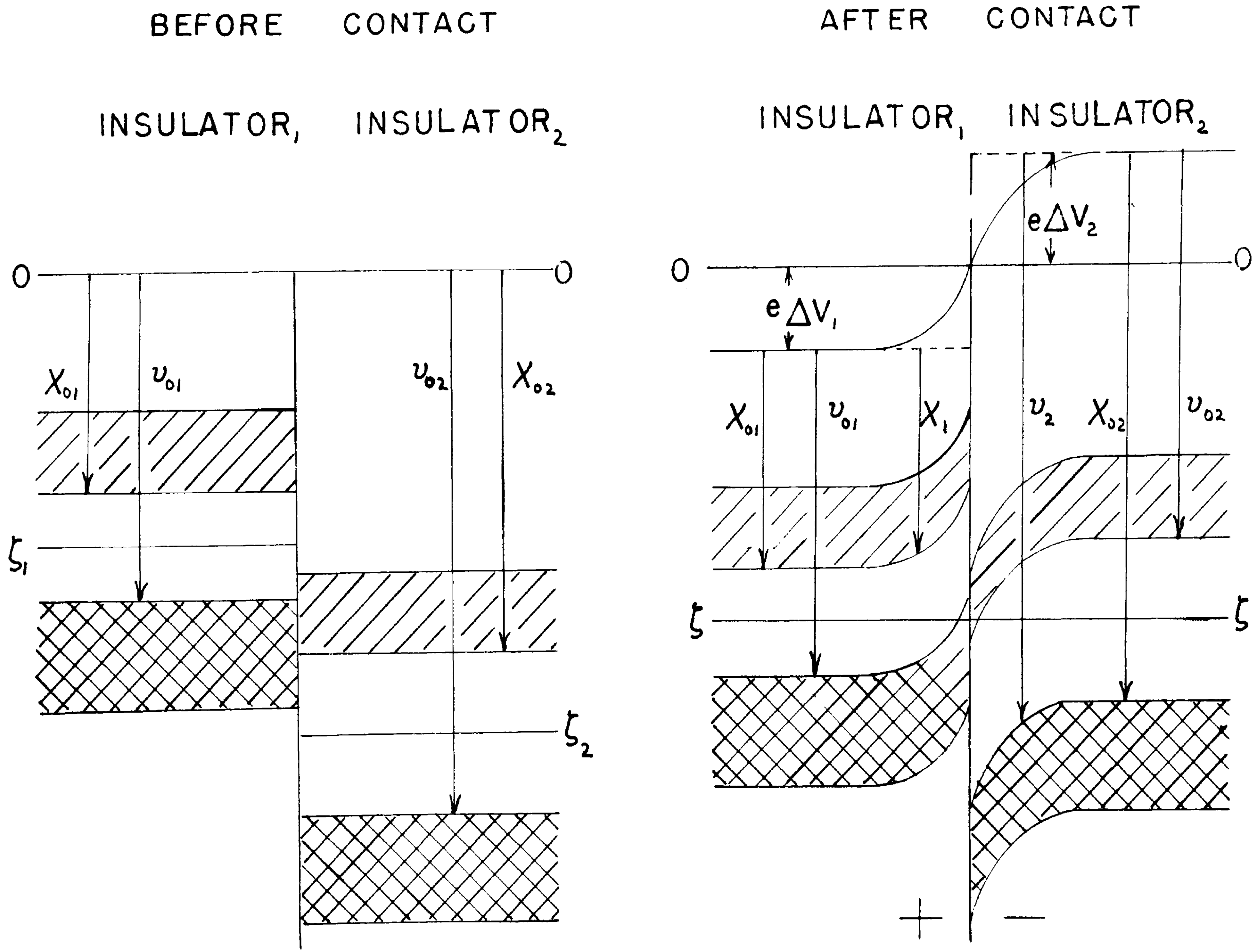

Figure 8. Schematic Energy-Band Diagram: Fermi Level of Insulator 1 above Fermi Level of Insulator 2, Top of Filled Band of Insulator 1 above Bottom of Empty Band of Insulator 2

(6) $V_{02} + e\Delta V_2 - y_{02} = \zeta$.

These equations, together with the requirement that at the boundary the field strengths must be equal, enable us to determine ζ, $e\Delta V_1$ and $e\Delta V_2$. We find, assuming the effective mass of the electrons in the two substances to be equal,

$$e\Delta V_1 = \frac{1}{2}(\chi_{02} - \chi_{01}),$$

$$e\Delta V_2 = \frac{1}{2}(V_{01} - V_{02}),$$

and $$\zeta = \frac{1}{2}(\chi_{02} + V_{01}) .$$

For a specific case let us take $\chi_{02} = -7 e.v.$, $V_{02} = -10 e.v.$, $V_{01} = -6 e.v.$, and $\chi_{01} = -4 e.v.$.

Then

$$\zeta = -6.5 \text{ e.v.},$$

$$e\Delta V_1 = -1.5 \text{ e.v.},$$

$$e\Delta V_2 = 2 \text{ e.v.}.$$

This case is illustrated in Figure 8.

Equations (1) and (3) for the volume charge densities for the two insulators are identical with those of Sections B and C of Chapter IV, respectively. The potential energy variations are identical with those of part 1 of Section B and Section 3 of Chapter IV. Therefore, we conclude that the volume and surface charge densities and depth of penetration of charge in the two insulators follow a form identical with those of parts 3 and 4 of Section B in Chapter IV.

CHAPTER VI

APPLICATIONS

A. Other Features of Contacts

Hersh and Montgomery[1] describe the experimental techniques and the results in a study on the static electrification of filaments rubbed against one another, and Harper[2] describes the charge transferred by spheres touching one another. In the previous chapters we have presented a quantitative account of the charge transferred when several types of contacts are made. At the present state of knowledge we cannot hope for a complete explanation of static electrification. Experimentally, the physical and chemical natures of the contacting surfaces are not known, nor are the temperature and the force at contact. Theoretically, we are not certain that the substances used possess the necessary periodicity for the application of the band structure of solids. However, we believe that some progress can be made, and we have approached the problem on the simplified picture that charge is transferred between two perfectly periodic structures and that part of the charge remains when separation occurs.

Our calculations were carried out under the assumption that the bodies in contact were in equilibrium. For metal-metal contacts equilibrium should be attained instantaneously, with a large charge per unit area of contact. In metal-insulator contacts, where electrons can spill freely from a filled band into an empty band, the transfer of charge near the interface should take place in a very short time. We see from Figures 2, 4, and 8 that owing to the smaller gap between the filled and empty bands of the insulator as compared with the other cases, an additional charge is furnished by thermal agitation to the empty band at large distances from the interface. The charge is small, but the gap is large enough that an appreciable time may elapse before equilibrium is attained. The cases represented by Figures 5, 6, and 7, where electrons are transferred from one body to the other by thermal agitation alone, should cause a long time to be required for equilibrium, with only small amounts of charge being transferred. We could expect appreciable charge in these cases only if the Fermi levels are nearly at the same level in the isolated substances or if the temperature is very high.

In our picture we assume that the charge which has been transferred remains localized at the point of contact in the case of insulators but not of course in metals. Experimentally, we know that charge can be localized on insulators; but theoretically an electron in the conduction band is free to move throughout the crystal upon removal of the attractive force due to the oppositely charged layer of the other substance. Gonsalves[13] has proposed a theory to explain localization based on surface states. Seitz [p.320-326] discusses localization from the point of view of imperfections on the surface, and Mott and Gurney [p.86-88, 124-131] put forth several models to trap electrons in the volume of the crystal. We merely say that some mechanism exists whereby electrons are immobilized within the volume of the insulators.

Harper[2] has made a study of the case of metal spheres as to how much charge remains upon separation. His results show that the fraction of charge remaining is practically independent of the speed of separation, amounting to perhaps one-half. The other half is returned by tunneling through the gap during the early portion of the separation. Harper does not consider in this respect any metal-insulator or insulator-insulator contacts, but it is clear that more charge will be tunneled back in these cases because of the greater intensity of field strength per unit area. Let us assume that perhaps one-tenth of the charge remains upon separation in the insulator-insulator cases. We now turn to comparison of our theoretical results with experiment.

B. Comparison with Experiment

A qualitative prediction of the theory is that a triboelectric series exists, that is, that substances can be ordered such that any substance above another substance in the series will become say positive when the two substances are rubbed together. This rule follows from the circumstance that the electrons flow from a substance with the higher to that with the lower Fermi level. Because the value of the Fermi level depends upon temperature, molecular structure, and state of strain as well as chemical composition, we can expect a definitely ordered series only if the state of each substance is carefully specified, or if we restrict ourselves to substances possessing well-developed Fermi levels. Triboelectric series are given in many places (see for instance reference 1). The existence of these series is evidence for some of the qualitative features of our picture.

Much more convincing evidence would be provided if we could predict the position of a substance in the series. Unfortunately we have almost no data on the positions of the energy bands in the substances used in the various experiments. Hersh and Montgomery (private communication) have made a start on predicting the values of certain of the energy parameters in the case of high polymers. They have been able to correlate the relative positions of several synthetic polymers in the triboelectric series with the properties of the monomers[14,15]. It is too early to say how meaningful this correlation is.

On the other hand, we may make use of the theory outlined in the earlier chapters of the present work to test our picture by a semi-quantitative procedure. We examine the sign and amount of charge transferred when a set of metals and insulators is rubbed against one another. Then we try to assign a set of values to the various energy parameters, and see if a consistent set of predictions is found. At the present stage of investigation the details of the mechanism of charge return--in particular the dependence upon resistivity--during separation are so little known that we must restrict ourselves to only a semi-quantitative treatment.

Figures 9a and 9b, reproduced from reference 1, Figures 26 and 29, show the experimental results of rubbing insulators on insulators and metals on insulators, respectively. We may correlate these results somewhat by the energy level scheme shown in Figure 10, where for the metals the photoelectric work function has been taken as the value for the Fermi energy. Agreement is obtained in every case with regard to the sign of charge transferred and in most cases with order of magnitude. The Fermi level for magnesium lies above the bottom of the nearly-empty band of nylon, and so a large charge is lost from magnesium to nylon. This case is discussed in Section B of Chapter IV. Aluminum has its Fermi level below the nearly-empty band and as explained in Chapter IV, Section D; a small charge is lost from aluminum to the nylon. The Fermi level for iron lies below that for nylon but not low enough so that electrons can spill from the filled band in the nylon to the iron and so, as studied in Section E, Chapter IV, a small number of electron is gained by the metal. For platinum we see that electrons may spill from the filled

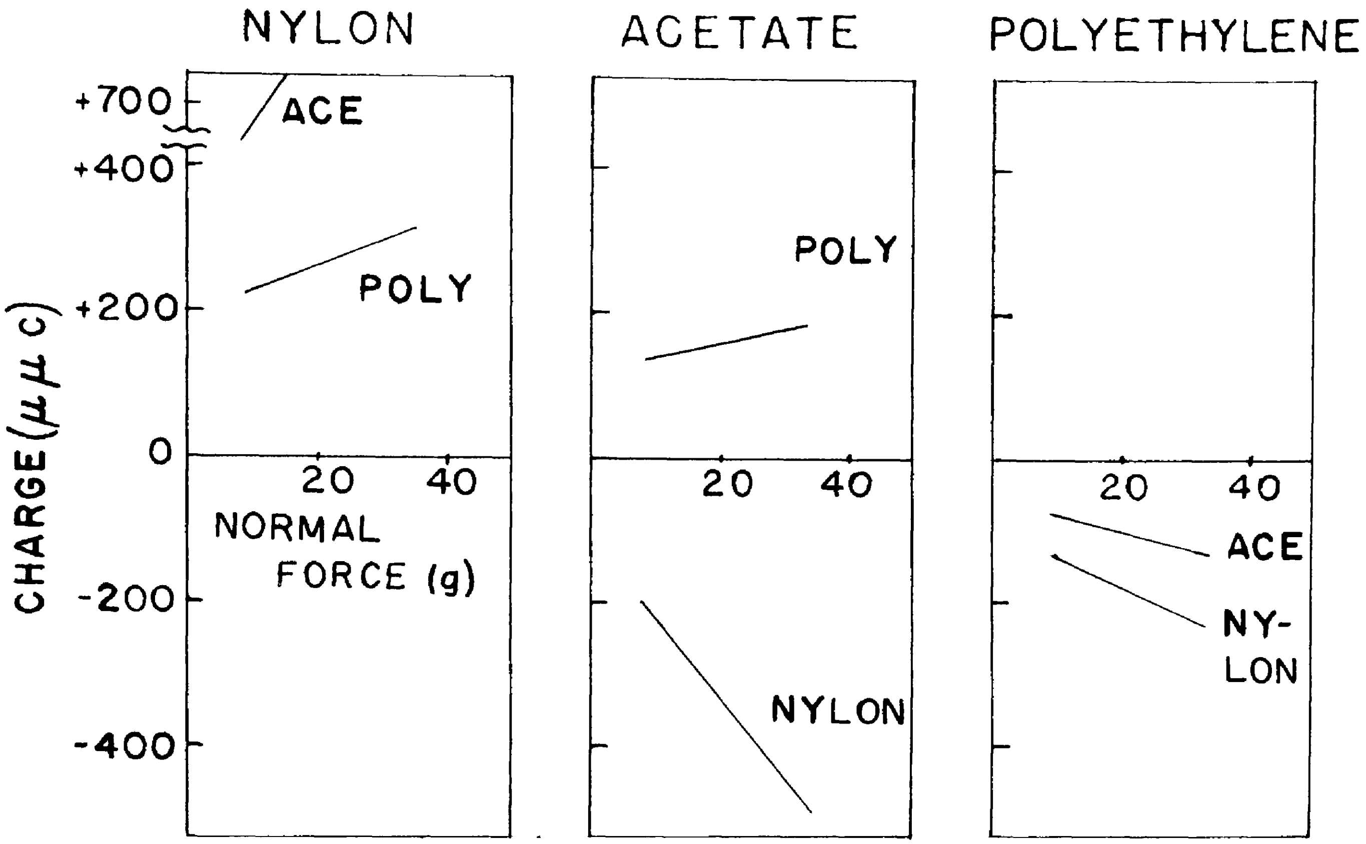

Figure 9a

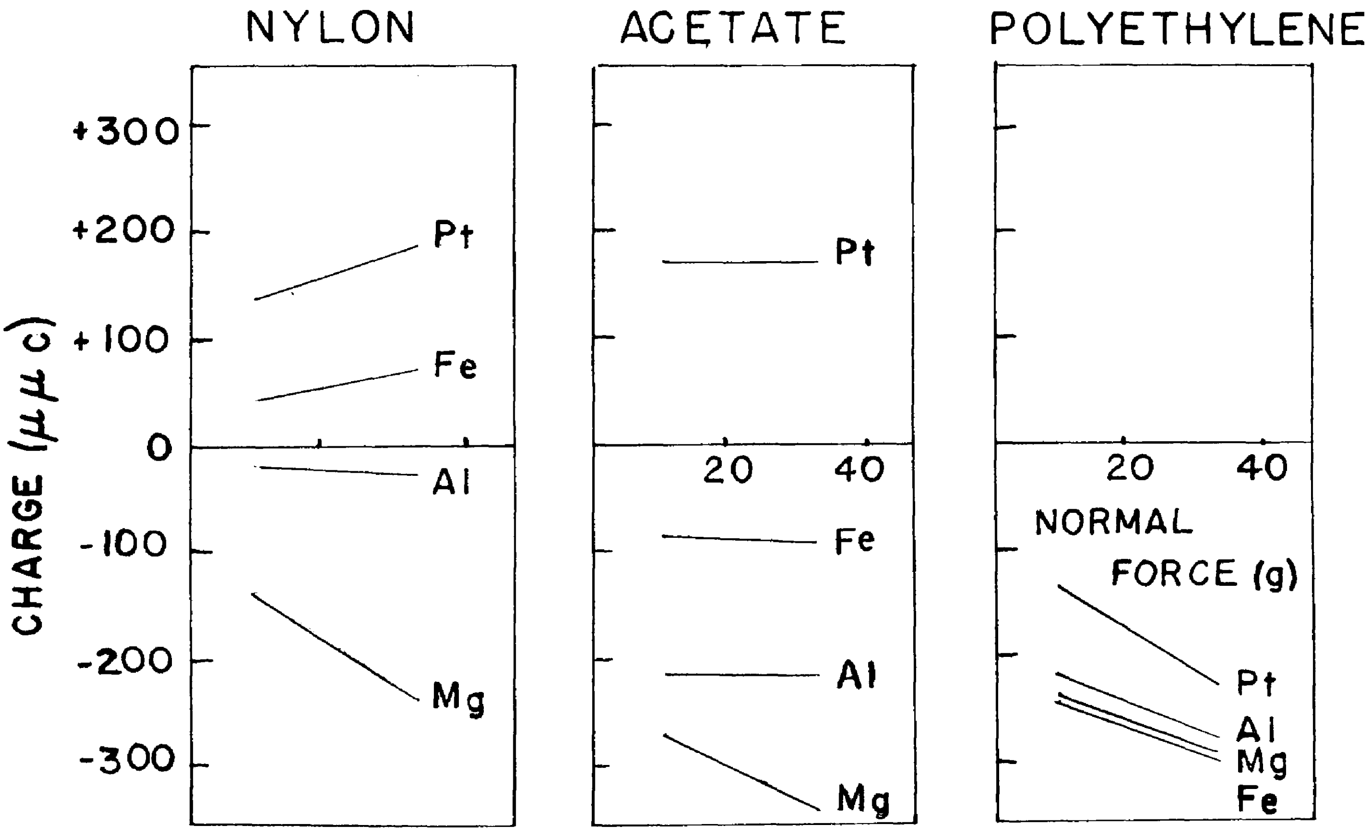

Figure 9b

Charge Transferred as a Function of Normal Force between Various Metals and Insulator Rubbed Together

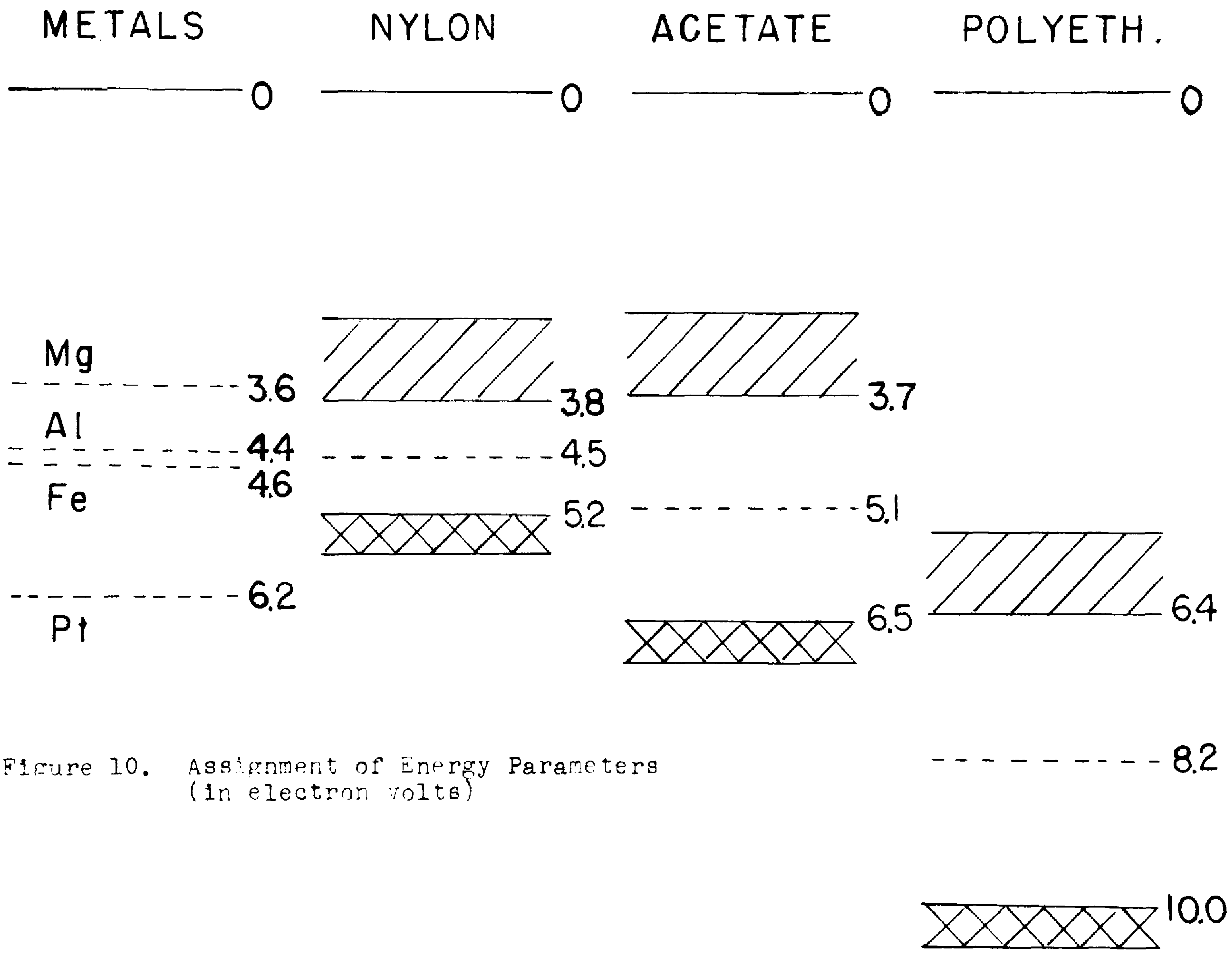

Figure 10. Assignment of Energy Parameters (in electron volts)

band of the nylon into the half-filled band of the metal and, therefore, as explained in Section C of Chapter IV, large charge is lost by the nylon to the platinum. We have one serious disagreement in our diagram, acetate on nylon. In this case we would expect a small charge transfer, as in Section B of Chapter V, but a large one is observed.

The data in reference 1 show that the maximum surface charge density measured is from 10 to 100 statcoulombs per square centimeter. Under normal conditions of temperature and pressure the breakdown strength of air corresponds to a surface charge density of 5 to 10 esu on a plane surface, and perhaps ten times this value for cylinders of the radius used in the experiments. According to our calculations in part 3 of Section B and part 2 of Section C of Chapter IV and Section C of Chapter V, we have densities of transferred charge of the order of 10,000 esu. Hence, we have an amount of charge transferred which is far more than adequate to explain the amount measured. The charge remaining is decreased by a factor of ten, say, through the tunneling effect, and finally by a factor of 10 to 100 through atmosphere breakdown. On the other hand, if the mechanism is that described in Sections D and E, Chapter IV, (electrons boiled up to an unfilled band), the maximum charge transferred over an energy gap greater than 0.5 ev is only 5.0×10^{-2} statcoulombs per square centimeter. The chief point to be established here is that large amounts of charge can be transferred even between insulators by the mechanism of Chapter V (electrons spilling into an incompletely full band) without calling upon local heating, or the existence of surface states. We cannot reach a more definite conclusion without additional experimental evidence on the position of the energy levels.

The same explanation would be valid for the results of Harper[2] on the light contacts of insulating surfaces with metals. Harper found that relatively large amounts of charge can be transferred when spheres of certain insulators are touched against spheres of various metals. These phenomena can be explained on the basis of the mechanism just discussed. On the other hand, when the insulator is an exceptionally good one, the charge measured is negligible. We believe that this finding can be explained by the large degree of reverse tunneling which must occur when the insulator is very good. For then the charge localized at the point of contact cannot flow away, and the resulting high field will produce a greatly increased tunneling. Of course, the energy band structure might be such that only small charge would be transferred, but Harper studied enough different insulators that it seems impossible for all of those showing little electrification to have the appropriate energy band structure.

CHAPTER VII

CONCLUSION

The theory put forth in the preceding chapters appears to be able to explain semi-quantitatively at least the basic phenomena in static electrification. Our results are adequate to explain the experimental results without invoking surface states. It is, of course, entirely possible that they do exist, and may even be the major cause of the charging process. The so-called "hot spots" proposed by Frenkel[16] likewise may exist, and are the primary source of charging in certain cases where a large charge is observed when a small one would be predicted on the basis of energy bands alone. It is evident that much more experimental evidence must be acquired before the proper choice can be made among the various theories.

The treatment could be refined by considering the problem in two or three dimensions[17], and by including exchange and correlation energies in the energy term for an electron in a solid. It is doubtful whether it is worth while to refine the treatment until additional experimental data on static electrificationare available or until there is more information on the actual values of the energy levels in the solids under consideration.

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