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THE QUANTUM CHEMISTRY OF ELECTRODE PROCESSES

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THE QUANTUM CHEMISTRY OF ELECTRODE PROCESSES

by Parbury P. Schmidt, Jr.

The purpose of this study is the formulation of a quantum mechanical theory of electrode processes based upon specific assumptions made concerning the nature of the electrode interface. As the thermodynamic and statistical mechanical approaches can give only limited information, it is necessary to resort to a quantum mechanical approach in the attempt to gain a more complete understanding of the problem.

In this work the method used to examine the nature of the charge transfer process at an electrode relies upon a model developed to represent the electrode interface. The assumptions about the interface upon which the model is based are rigorously defined. Specifically, it is assumed that next to the electrode surface there is at least one layer of neutral adsorbed solvent molecules which exhibits an order resembling solid state order. Interspersed throughout the ordered layer of solvate molecules are the reactant ions. The process of charge transfer is assumed to be dependent directly upon orbitals of the solvate molecules. The transfer of an electron is assumed to proceed, first, by a transition from the electrode to the solvate molecule, and, second, by a transition from the solvate molecule to the ion. For this model general conclusions are drawn concerning the rates of the electron transfers leading to the currents measured.

The discussion proceeds next to a specific quantum mechanical examination of the interfacial state, and then to an analysis of

possible mechanisms of charge transfer within the interface. The quantum mechanical description is based upon the representation of the electrode interface as a surface complex made up of the electrode surface atoms, the solvate molecules, and the ions. Rate-determining charge transfer transitions leading to the currents are considered only within the surface complex. The energy needed to effect the transitions must be transferred from the surroundings. An examination of several possible means of energy transfer with the surface complex leads to the explicit expressions for the currents.

In addition to the mechanism involving the direct participation of the intervening solvent layer in the charge transfer process, direct charge transfer between the reacting species and the electrode is also possible. Such a situation is treated by considering the surface complex to be a type of simple charge transfer complex between the reactant species and the surface metal atoms of the electrode. The charge transfer transitions leading to the currents are the charge transfer transitions within the complex.

Electrodeposition is treated by assuming the formation of solvated atoms in the electrode interface which then undergo free radical-like encounter reactions with the electrode surface. Electrodissolution, on the other hand, is treated by assuming a partially solvated site on the metal surface. The current is then dependent on the rate at which the partially solvated surface atom breaks away from the surface.

Finally, as a result of the assumption of a surface complex

along with the assumption of real transitions within the surface complex responsible for the process of charge transfer, it is shown that it may be possible to excite individual transitions through the use of an external light source. The electrode photoeffect would be expected to show a spectrum of the charge transfer transitions in the surface complex for a plot of the current versus the wavelength of the exciting light. Conclusions are also drawn concerning the expected nature of the spectroscopic examination of the interface using internal reflectance spectroscopic techniques.

To Carol

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CHAPTER I

INTRODUCTION

The presence of an electrode in a solution of an electrolyte which is a redox system allows for the possibility of heterogeneous electron exchange between the two phases. In recent years investigators--both theoreticians and experimentalists--have demonstrated keen interest in seeking detailed explanations of the process of charge transfer.[1] This interest is prompted simultaneously by the realization that classical arguments from thermodynamics and statistical mechanics fail to give the whole picture, and by the emergence, since the Second World War, of new experimental techniques. These techniques enable the investigator to follow the course of charge transfer reactions in solution by "tagging" ions of interest and following their fate. As the charge transfer itself does not involve bond-breaking, it is particularly appealing to the theoretician. Before examining the new aspects of the theory of charge transfer to be presented in this work, it is of interest to examine the progress made in electrochemistry thus far.

The condition of thermodynamic equilibrium requires that there be no excess charge in the total interface, that there be equality of the chemical potential in both phases, and that the current in one direction equals the current in the reverse direction (exchange current).

Within the interface there there exists a difference in the chemical potential between the two phases. This potential difference presents a potential barrier through which, or over which, the electron must pass in getting from one phase to the other.[2]

The presently accepted model of the electrical double layer formed at the interface of the electrode and the electrolyte consists in part of an oriented neutral adsorbed layer of solvent molecules which is at least one monolayer thick (in the absence of specific adsorption of the ions of the electrolyte).[3] The distance of closest approach of a charged ionic species to the electrode is at the plane of the adsorbed neutral monolayer. The Gouy-Chapman theory, with modifications due to Stern, Frumkin, and others,[3] predicts the potential and the differential capacitance in the double layer as a function of the distance from the electrode plane. The Gouy-Chapman theory, which is closely allied to the Debye-Hückel theory, is based on the following assumptions.[3] First, it makes use of the Poisson equation,

$$\nabla^2\phi = -4\pi\rho/\epsilon , \qquad (1)$$

giving the relation between the potential and the charge distribution. Second, the work, w^x_i, necessary to bring an ion, i, from infinity to a distance x from the electrode surface gives a concentration of the ion at x in the form

$$n^x_i = n^s_i \exp(-w^x_i/kT) , \qquad (2)$$

where n^s_i is the concentration of ion, i, in the bulk of the solution. The density of charge appearing in equation (1) is

$$\rho_x = \sum_i z_i e_o n^x_i = \sum_i z_i e_o n^s_i \exp(-w^x_i/kT) \qquad (3)$$

(e_o is the unit of elemental charge). Substituting equation (3) into the one-dimensional form of equation (1) and integrating gives a result from which one can find the differential capacitance and the charge of the electrode.

The Gouy-Chapman approach is based on the assumption that the electrode is regarded as a parallel plate capacitor. The original treatment made use of the approximation of point charges which, of course, leads to error. The same treatment is improved by allowing for the finite size of the ions, and in addition, allowing for adsorptive effects. Inclusive of all modifications, the theories based on the original Gouy-Chapman treatment remain classically electrostatic with respect to the electrical potentials, and classically thermodynamic with respect to any work expended in the formation of the double layer. Hence, such macroscopic quantities as the charge on the electrode and the associated potential can be realized. The treatment reveals the dependence of the processes on the electroactive ions and the effect of adsorption of both ions and neutral species in solution. This, of course, is a great accomplishment, and much information about the nature of the electrode interface is gleaned from it.

However, much of the information gained comes about through inferences made about double layer structure on the basis of the observation of gross properties.

The analysis of the electrode system is best started from an equilibrium point of view. This is precisely the approach of the Gouy-Chapman theory. From it one can, in principle, obtain the equilibrium potential measurable at an electrode. The question naturally arises, what is the effect of varying the potential by the imposition of some external potential different from the equilibrium potential. The well known effect is the appearance of a net current, or flow of charge through the system. To analyze this situation the following reaction sequence is examined[4,5]

$$O + ne_o \underset{k_{r,h}}{\overset{k_{f,h}}{\rightleftharpoons}} R, \tag{4}$$

where O represents the oxidized species, R the reduced species, and e_o the elemental charge. The forward and reverse heterogeneous rate constants respectively are $k_{f,h}$ and $k_{r,h}$. These rate constants are related to the absolute rate constants through the relations

$$k_{f,h} = k^{\circ}_{f,h} \exp(n\alpha \mathcal{F} \mathcal{E} /RT),$$

$$k_{r,h} = k^{\circ}_{r,h} \exp(-(1 - \alpha)n \mathcal{F} \mathcal{E}/RT) \tag{5}$$

where α is the transfer coefficient, n the number of charges transferred, $\mathcal{E}$ the electrode potential, and $\mathcal{F}$ the Faraday

constant. The rates of change of the concentrations of oxidized and reduced species are given by

$$- d[O]/dt = d[R]/dt = k_{f,h}[O] - k_{r,h}[R]. \quad (6)$$

From (6) the current is $I = n\mathcal{F}d[R]/dt = - n\mathcal{F}d[O]/dt$. Thus, from equations (5) and (6) the total current is given by

$$I = n\mathcal{F}\left(k^{\circ}_{f,h}[O] \exp(n\alpha\mathcal{F}\mathcal{E}/RT) - k^{\circ}_{r,h}[R] \exp(-(1 - \alpha)n\mathcal{F}\mathcal{E}/RT)\right). \quad (7)$$

As has been mentioned in a previous paragraph, the condition of equilibrium requires that there be no net current; thus $I = 0$, and from equation (7)

$$\Delta\mathcal{E} = (RT/n\mathcal{F})\ln(k^{\circ}_{f,h}/k^{\circ}_{r,h}) + (RT/n\mathcal{F})\ln(C_{ox}/C_{red}) \quad (8)$$

which is the Nernst equation. The exchange current is given either by

$$i_e = k^{\circ}_{f,h}[O] \exp(n\alpha\mathcal{F}\mathcal{E}/RT) \quad (9)$$

or

$$i_e = k^{\circ}_{r,h}[R] \exp(-(1 - \alpha)n\mathcal{F}\mathcal{E}/RT) \quad (10)$$

which are equal to each other.

Imposing upon the electrode an external potential

different from the equilibrium potential yields, of course, a net current, $I \neq 0$.

The evaluation of the absolute heterogeneous rate constants appearing in equations(5), (7), (9) and (10) by suitable means is the ultimate purpose of the study of electrochemistry. Means exist for their experimental determination both at equilibrium and nonequilibrium conditions.[6-13] Thus, any theoretical evaluation can ultimately be subjected to the test of experimental comparison.[14] The absolute rate constants provide the link between gross observation and microscopic occurence. This is so because the rate constant is a measure of the dynamics of the system. By careful control of experimental conditions the rate constant is made to reveal a minimum number of occurances connected with the charge transfer. By prescinding all extraneous effects, such as mass transport, it is possible to reveal chemical and electronic dependences on which the rate constant may depend. It is through the process of excluding all effects except the one of interest for a particular investigation that one eventually obtains a knowledge of the microscopic event. Ultimately, because many phenomena are directly unobservable, models must be constructed and examined on a theoretical basis to see if the gross properties of the system can be related to that which might be conceived to happen microscopically. In addition to the test of direct experimental correlation to theory, there is a corollary test in that from

the model one should be able to connect related phenomena, and possibly, but not necessarily, predict new phenomena.

Considering now the process of electron transfer from an electrode to an electroactive species in solution, it is of interest to review in a more or less chronological order the development of models to explain the process. The process of electron transfer is dependent upon either chemical or electronic effects. Naturally, if the electron transfer between the electrode and electroactive species is very much faster than the migration of electroactive species to the electrode surface, then the overall process of electron transfer is governed by chemical and mass transfer factors. The mass transfer factors have been extensively treated for almost any conceivable electrode configuration along with the assumption of different forms of diffusion processes responsible for the migrations of reactants and products in solution, e.g. ionic, thermal, and mechanical diffusion. If, on the other hand, chemical effects are minimal--for example, an equilibrium situation--then electronic effects are presumed to dominate the chemical effects. The rate constants are thus a measure of the charge transfer. However, the process of charge transfer may not be solely dependent upon electronic migration through the interfacial system at an electrode, but may also depend strongly upon vibrational and other factors within the individual electroactive species. These additional factors are chemical factors which contribute a part to the overall electronic energy

description of the system. It is the dependence of the rate constant upon such factors as solvent sphere reorganization and others which has captured the attention of theoreticians and experimentalists in recent years.

Gurney[15] has treated the passage of the electron from one phase to the other through the potential barrier on the basis of a tunnel effect. Gerischer[2] has extended the treatment and presented current expressions for the simple reaction of the type

$$M^{(z+1)+}.\text{solv.} + e^-_{\text{metal}} \rightleftharpoons M^{z+}.\text{solv.}$$

From the above reaction the density of states of the occupied and unoccupied levels in the solvated ions can be determined by the work involved in converting one form to the other. The work needed to bring an electron from infinity and place it in solution to occupy the lowest state without change in the solvate structure defines the energy of the unoccupied states. The requirement that the solvate structure does not change is a result of the Franck-Condon principle. The energy levels of the occupied states are defined by the reverse process--that being the work needed to remove an electron from the solvated ion, without change in the solvate structure, and the subsequent removal of the electron to infinity.

Each ion in solution is surrounded by solvent molecules which are associated with the ion through ion-dipole and other interactions. Due to thermal agitation the solvation

structure can fluctuate, and the distribution of solvate structures can be represented by a Boltzmann distribution. With each structure of the solvated ion there is a corresponding energy state in the redox system, and hence, the density-of-states functions for the redox system.

As the electron transfer process at the electrode is radiationless, the condition for tunneling is that the electron makes transitions between equi-energetic states in the electrode interface. If the density-of-states functions for the redox system are signified by $D_{ox}(E)$, $D_{red}(E)$, and the density-of-states functions for the metal electrode by $N_o(E)$, $N_u(E)$ for the occupied and unoccupied levels, respectively, the expressions for the total cathodic and anodic currents are given by[2]

$$j^- = e_o \int_{-\infty}^{+\infty} \nu^-(E) N_o(E) D_{ox}(E) dE \qquad (11)$$

and

$$j^+ = e_o \int_{-\infty}^{+\infty} \nu^+(E) N_u(E) D_{red}(E) dE, \qquad (12)$$

where $\nu^-(E)$ and $\nu^+(E)$ are the penetration coefficients in the anodic and cathodic directions, and e_o is the electronic charge. By using the density-of-states functions for the redox electrolyte defined above, Gerischer has shown that an electron in that system obeys the Fermi-Dirac statistics, and further that the Fermi level of the redox system is defined by[2]

$$E_{F,redox} = {}^{o}E_{F,redox} + kT \ln (C_{red}/C_{ox}), \qquad (13)$$

where ${}^{o}E_{f,redox}$ is defined as the energy difference between the ground state vibrational reduced ion level and the ground state vibrational oxidized ion level.

Although the barrier penetration model predicts the mode of the overall electron transfer, it does not account explicitly for the effect of the geometry about the ion, nor does it account explicitly for the individual effect of the energy levels within the solvent upon the magnitude of electron transfer across the interface.

In addition to the work of Gerischer,[16,17] works by Hush,[19-22] Marcus, Levich, Dogonadze and Chizmadzhev[23-28] have also dealt with charge transfer at electrodes. The approaches taken by these authors bear resemblance to one another. They are all based on a collisional approach which leads to an evaluation of the progress of the reaction along a reaction coordinate. This approach is the application of the absolute reaction rate theory of Eyring to electrode processes, done, however, in a novel and elegant manner. For the most part, the treatment of electrode charge transfer by these authors has followed similar treatments by them of the problem of charge transfer between reductant and oxidant in solution: homogeneous charge transfer reactions.[16,17,22,25-28,29,30]

In one form or another, all the methods have in common the treatment of the reorganization of the solvate spheres

about the reactant ions upon charge transfer. The charge transfer process is envisioned to involve motion along a reaction coordinate to a point at which there is an activated state. This activated state is given as the point at which the two potential energy curves or surfaces, one for reactants and one for products, intersect.[1] At the intersection there is a splitting (see Figure 1). Depending upon the nature of the reaction, it will either be adiabatic, or non-adiabatic; i.e., the reaction will either proceed along the lower unbroken curve, or it will jump from one solid curve to the other on passing through the intersection region. Adiabaticity is usually realized when the system approaches the intersection region with low velocity. Under these conditions, the electrons of the reactants have--under the dictate of the Born-Oppenheimer approximation--the ability to "follow" the nuclear motion. Thus, at the intersection the system remains on the lower curve.

The treatments all consider the intersection of the potential surfaces. The importance of solvent reorganization lies in the attempt to determine the nuclear configuration states, and to determine the probability of electron transfer at these configurations. These configurations are assumed to be in thermal equilibrium with the remaining configurations from which electron transfer can take place.

The treatment of Hush[16-18] is adiabatic. That of Marcus[1,19-22,29,30] leaves the question of adiabaticity

Figure 1

Profile of the potential energy surface for the reactants and products (R and P respectively) plotted versus some generalized reaction coordinate--usually the nuclear configuration (after Marcus, reference 1).

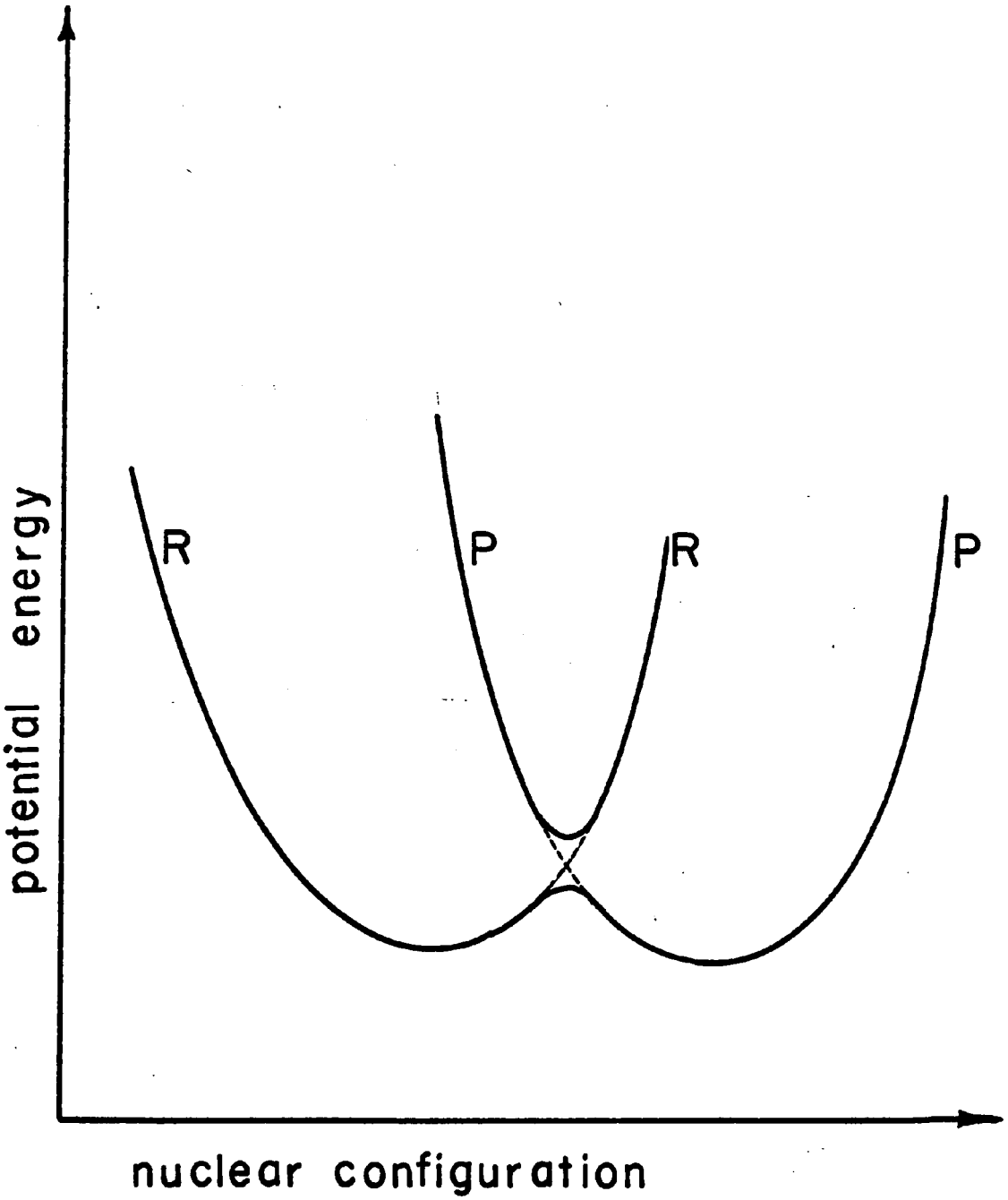


Figure 1

open, while that of Levich et. al.[23-28] is non-adiabatic. Hush argues that there is no reason why an adiabatic approach is not most probable. He bases this argument on the observation that the reaction

$$Fe^{+3} + Cl^{-} = FeCl^{+2}$$

is adiabatic in the sharing of charge between the chloride and ferric ions.[17] However, Marcus has indicated the probability that non-adiabaticity may be the more dominant property.[31] The question of non-adiabaticity is dependent on the strength of the interaction.[1,25] Levich et. al. assume a weak interaction, and thus treat the transfer problem in perturbation theory formalism. This leads to the non-adiabaticity. It is assumed that the outer coordinate sphere reorientation--reflected through the polarization of the dielectric continuum--dominates; the inner coordinate sphere remains virtually unaltered. Hush,[17,18] on the other hand, considers reorientation of the inner coordination sphere along with the polarization of the continuum. This yields his adiabatic transfer. Finally, Marcus has presented a statistical mechanical treatment which relies on the evaluation of the Arrhenius frequency factor to resolve the difficulties.[22]

The rate expressions obtained by Marcus have the form[1]

$$k_{rate} = \kappa \rho Z \exp(-\Delta F^*/kT). \qquad (14)$$

The free energy of activation contains terms in the work necessary to bring the reactants together from infinity to a mean separation distance, and the work to remove the products to infinity. It contains terms for the inner and outer sphere contributions to the changes in coordinates of the coordination shells, and a standard free energy of reaction. The evaluation of changes in the coordinate shells is worked out on a dielectric continuum basis, and has much in common with polaron theory. In addition, in expression (14) Z is the approximate number of collisions between reactants in a unit area of the electrode surface. The factor ρ is the ratio of the root mean square fluctuation at the mean separation in the activated complex to the root mean square fluctuation of a coordinate at infinity (i.e., away from the intersection region). The velocity weighted average of the transition probability from a given R surface to a given P surface is K .

More recently, papers by de Hemptinne[32] and by Schmidt and Mark[33] have dealt with the electron transfer from the point of view of what is best described as a "dynamical equilibrium" approach. Since the work of Schmidt and Mark is the subject of this thesis only de Hemptinne's work will be considered in this introductory review. The approach taken by de Hemptinne is an extension of the original work of Gerischer,[2] mentioned earlier. De Hemptinne assumes that at the electrode there is a reaction of the type[32]

$$O + e^- \longrightarrow R^*$$

$$R^* \longrightarrow R + \text{energy}.$$

There is thus implied an equilibrium distribution of reactants at the surface. The reactants are held at the surface and in their equilibrium configurations by adsorptive forces. The electronic motion is much faster than the nuclear motion, and the perturbations leading to the transfer are contained in the adsorption Hamiltonian. Once an electron is transferred, the product of this transfer is energetically out of balance with the equilibrium arrangement and must relax, or stabilize, to give the final product; this is indicated by the second step above. The approach of de Hemptinne has been recently critized by Hale[34] who claims that the electronic transition makes use of a "hot" electron, and as such is not a "most probable" transition. Although de Hemptinne's approach tacitly implies the equilibrium situation at an electrode, with all reorganization energies reflected in the adsorption Hamiltonian, Hale seems to have missed this point. The confusion seems to arise from Marcus' insistance[1] that non-adiabatic transfers must be considered by solving the Schrödinger equation for electronic-nuclear motion, which, he claims, necessitates the use of potential energy diagrams such as seen in Figure 1. Marcus does point out[1] that from a tunnelling model the calculation of the transmission coefficient serves as a crude method of evaluating the

splitting at the intersection region. The barrier for the tunnelling is not, however, the barrier represented in Figure 1. The height of the barrier must be the same energetically as the energy necessary to move along a potential energy surface to an intersection point. The width of the barrier for an electroactive species in an equilibrium interfacial situation is not inordinately great (i.e., it is not as great as the barrier between the electrode and a free electroactive species in the bulk of the solution). Hence, the tunnelling rates are reasonable. As the height of the barrier is also not inordinately great, the electron transfer is considered equally well by making use of transitions over the barrier involving either virtual or real electronic levels. Such an approach as this can yield more information about the electrode system, and thus has its own value. It is not a crude means of evaluation of the splitting at the intersection region, but an exact means of obtaining a clearer mechanism of the process of charge transfer. It can emphasize the individual contributions of all segments of the system.

In the following chapters a specific model of the electrode interfacial system will be presented. A detailed analysis of the consequences of the assumption of the model will be shown to lead to a better understanding of the mechanism of electron transfer at an electrode. Finally, it will be shown that by assuming model molecular systems for the interfacial state, predictions can be made

concerning relations between different electrode reactions, and predictions can be made of the possible existence of new electrode phenomena.

CHAPTER II

MODEL OF THE ELECTRODE INTERFACIAL SYSTEM

In constructing a molecular model for the electrode interface which will explain the mechanism of electron transfer, it is assumed that there is molecular order resembling solid-state order in the neutral solvate species which, in the absence of other more preferentially adsorbed substances, makes up the neutral adsorbed layer.[33] This molecular order is assumed to extend from the electrode surface several monolayers out into the bulk of the solution. The order which is assumed to exist at the electrode will vanish rapidly as one moves away from the electrode. The matrix of ordered solvate molecules at the electrode makes up the basis of a semiconducting material with the associated formation of conduction and valence states in the matrix. The ions to be reduced or oxidized occupy sites in the ordered matrix and behave as impurity sites.

The semiconductor analogy is limited, however, because the dimensions of the ordered system extending out from the electrode are small. Thus, the direct application of the current expressions for the solid-state situation to electrode phenomena will break down and one must resort to a more limited approach to the problem. The approach to to be taken is to consider the detailed order of the solvent molecules and ions at the electrode surface and then to consider the stepwise transference of the electron

through the regions in the interface which presently are defined. The choice of model to be used has been prompted by the experimental work of Mark and others[35-40] which indicates the participation of solvate and coordinating ligands in the process of charge transfer. (In addition, recent work of Heyrovský on the electrode photoeffect also substantiates the participation of solvate in charge transfer.[41,42])

Considering the detailed arrangement of the species in the ordered layer making up the interface, the assumption is made[33] that the nature of the order is determined as a result of the combination of three factors. These three factors are (i) the adsorptive and (ii) electrostatic fields in the interface, and (iii) the geometry or coordination of the solvate molecules around the ions in the bulk of the solution. In the interface the order assumed by the solvate molecules and the ions is that order which minimizes the lattice energy under the equilibrium conditions dictated by some equilibrium rule. This equilibrium rule determines the ratio of reactant to product ions in the interface, viz., oxidized to reduced species. The geometry of the solvate spheres about the ions in the bulk of the solution is in effect an initial condition in determining the type of order of the species at the electrode. It is reasonable to assume that the coordination of the solvate sphere of the ion in excess under an equilibrium concentration for the entire system exerts the greatest influence upon the order

of the species in the interface. For the special equilibrium condition of equal concentrations of all ionic species, the order assumed at the interface is dependent upon the relative coordination energies of the ionic species. The coordination of that species having the lowest bulk-solution--solvate-sphere coordination energy predominates. Although the same for both ionic species, the coordination of the solvate spheres at the electrode is not the same as the coordination found in the bulk of the solution, due to the combined effect of the adsorptive and electrostatic fields.

The process of forming the interface requires that the solvation spheres about the ions must change, as indicated, in order that the ions be incorporated into the ordered layer. With the above assumptions, and the requirement of energy change, one is lead to the conclusion that the system electronic energy level differences in the interfacial state will be manifest in the activation energies which are the same as those found from the exchange current. This is so because the energy"effects", i.e., the changes on interfacial state formation, are reflected in the activation energies through the system Hamiltonian. There thus exists a certain definite energy which an electron must acquire to surmount the "barrier" between the electrode and the ion. The essential point to be emphasized is that once the initial energy necessary to form the interfacial system is spent, no more energy, on a time and space average,

need be expended. This is so as long as the system remains in an equilibrium state.

Under nonequilibrium conditions the formation of an excess of either the oxidized or reduced species in the ordered layer creates a condition whereby an attempt is made by the system to regain the equilibrium distribution. Thermal energy from the bulk of the solution can be exchanged with the ordered layer to change the solvate structure of the product species, which has just gained or lost an electron. This causes ordered layer breakdown with subsequent departure of the product ion surrounded by solvate molecules with the coordination characteristic of that ion in the bulk of the solution. Once a product ion--with its new solvate structure--leaves the electrode, another ion can move in and change its solvation sphere to assume the equilibrium coordination found at the electrode. Under these conditions the kinetics of the reactions at the electrode can become dominated by chemical and mass transport factors. Energy is expended in this process, but only until the system adjusts to the applied potential and assumes the equilibrium dictated by it.

As it has been assumed that the ionic species at the electrode-solution interface preserve a solvation environment, it is reasonable to expect that the neutral adsorbed layer of solvent molecules next to the electrode corresponds to a part of the solvation structure around the ions in the interface. It is further assumed in the treatment that

the metal--metal-ion association--which would be the case if the ions reacted directly at the metal surface of the electrode--does not take place. (This is in opposition to the model chosen by de Hemptinne[32] who assumes that the solvation sphere about the reactant ions is hemispherical. This would then imply direct reaction; the effect of solvate is reflected merely in the ionic energy levels.) Establishing these conditions leads to a model for the electron transfer across the interface which can best be represented by analogy to the charge transfer mechanism in spectroscopy.[33] With such a model two charge transfer transitions need to be considered. The first takes the electron from the electrode to the solvent sphere of the ion, and the second, from the solvent sphere of the ion to the ion itself. Under most circumstances the transitions are radiationless.

It is possible to discuss in a general manner, without specific reference to wavefunctions in the system, the kinetics of the charge transfer. It is necessary only to specify that there is an intermediate state of the system which is accessible from either the electrode or the ion. This intermediate state is assumed to be a charge transfer state of both the ion and electrode. It is furthermore assumed that the charge transfer state lies higher in energy than either of the other states.

Denote by O, I, and R respectively, the oxidized, intermediate, and reduced species in the electrode interface. The forward, or cathodic current depends on the

rate of appearance of R. The starting condition for the forward current is the equilibrium concentration of O, $[O]$, and it indicates the situation where the electron is still bound to the metal electrode. The state I, the intermediate state, specifies the situation whereby the electron has been transferred from the metal to the solvate layer. Finally, the state R denotes the reduction accomplished by the transfer of the electron from the intermediate to the ion. Very simply, these steps are represented as follows:

$$O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} I \qquad I \xrightarrow{k_3} R.$$

(The forward current depends upon the population of I as a result of transitions from O, hence k_4 does not appear.) The steady state approximation, $d[I]/dt = 0$, gives

$$[I] = k_1/(k_2 + k_3)[O]. \tag{1}$$

The current is a function of $d[R]/dt$, and from the above one finds that

$$i_f \propto d[R]/dt = k_1k_3/(k_2 + k_3)[O]. \tag{2}$$

Distinguish now between four limits in the relations between the rate constants.

The first, $k_2 < k_3$, leads to the simple expression

$$k_{rate} = k_1 \tag{3}$$

by ignoring k_2. The second, $k_2 > k_3$, gives

$$k_{rate} = k_3(k_1/k_2) = K_{eq(1)}k_3. \quad (4)$$

Third, noting the case in which $k_2 \simeq k_3 > k_1$ it is seen that the rate constant becomes

$$k_{rate} = k_1/2. \quad (5)$$

Finally, if $k_2 \simeq k_3 < k_1$, then from equation (1), $[I] = K'_{eq(1)}[O]$, and the rate constant is

$$k_{rate} = K'_{eq(1)}k_3. \quad (6)$$

The first and third cases lead to a rate constant dependent on the rate of transition of the electron from the metal to the intermediate level. The second and fourth cases are dependent on the rate of decay from the excited intermediate to the final ionic level. For the second and fourth cases, it is convenient to consider the K_{eq} given by some distribution function; in most cases this is a Boltzmann distribution in the low temperature limit.

Identical arguments follow for the consideration of the reverse current. Add now the reverse transition, $R \xrightarrow{k_4} I$. With respect to the reverse current the steady state approximation gives

$$[I] = k_4/(k_2 + k_3)[R]. \quad (7)$$

The reverse current is proportional to

$$i_r \propto d[O]/dt = k_2k_4/(k_2 + k_3)[R]. \quad (8)$$

The four limiting cases applied to the reverse current rate constants give: One, for $k_2 < k_3$,

$$k_{rate} = k_2(k_4/k_3) = K_{eq(2)}k_2. \quad (9)$$

Two, for $k_2 > k_3$,

$$k_{rate} = k_4. \quad (10)$$

Three, for $k_2 \simeq k_3 > k_4$,

$$k_{rate} = k_4/2. \quad (11)$$

Finally, for $k_2 \simeq k_3 < k_4$,

$$k_{rate} = K'_{eq(2)}k_2. \quad (12)$$

The evaluation of the rate constants for the currents depends upon the nature of the perturbation in the whole system assumed responsible for the transitions. The problem can be approached from the standpoint of both time-independent and oscillatory perturbations. In addition, due to the complexity of the interfacial system there are many possibilities for the transfer of energy from sub-systems surrounding the surface complex. The specific evaluation of the perturbations leading to the transitions is the subject of a later chapter. For the purposes of this chapter, however, it is sufficient to consider the surroundings as being a source of energy through some

field quantity, oscillatory in time, such that the current expressions can be expressed in the Einstein transition coefficients. To do this, note is made of the low temperature approximation of the radiation density

$$\rho(\omega_{mn}) \cong A_{nm}/B_{nm} \exp(-E_{mn}/kT). \tag{13}$$

The relation (13) is the result of the low temperature limit either for a Fermi-Dirac, or a Bose-Einstein distribution. Thus, for the general discussion, it is unnecessary to specify the symmetry properties of the field quantity. Keeping in mind the principle of detailed balancing, the current expressions for the four limiting cases become: One, case 1(a)

$$i_f = A\mathfrak{F}C_{ox}B_{oi}\rho(\omega_{oi}) \cong A\mathfrak{F}C_{ox}A_{io} \exp(-E_{oi}/kT)$$

$$i_r = -A\mathfrak{F}C_{red} \exp(-E_{ri}/kT)\left[B_{io}\rho(\omega_{oi}) + A_{io}\right]$$

$$\cong -A\mathfrak{F}C_{red}A_{io} \exp(-E_{ri}/kT), \tag{14}$$

where the rate of induced relaxation is assumed to be much less than the spontaneous relaxation. For the opposite situation, the induced transition greater than the spontaneous, we have--case 1(b)--

$$i_r \cong -A\mathfrak{F}C_{red}A_{io}\exp[(E_{ri} + E_{oi})/kT. \tag{15}$$

Two, case 2(a)

$$i_f = A\mathfrak{F}C_{ox}\exp(-E_{oi}/kT)\left[B_{ir}\rho(\omega_{ri}) + A_{ir}\right]$$

$$\cong A\mathfrak{F}C_{ox}A_{ir}\exp(-E_{oi}/kT)$$

$$i_r = -A\mathfrak{F}C_{red}B_{ri}\rho(\omega_{ri}) \cong -A\mathfrak{F}C_{red} \times A_{ir}\exp(-E_{ri}/kT), \quad (16)$$

case 2(b),

$$i_f \cong A\mathfrak{F}C_{ox}A_{ir}\exp(E_{ri} + E_{oi})/kT. \quad (17)$$

Three, case 3,

$$i_f = A\mathfrak{F}C_{ox}B_{oi}\rho(\omega_{oi})/2 \cong A\mathfrak{F}C_{ox}A_{io}\exp(-E_{oi}/kT)/2$$

$$i_r = -A\mathfrak{F}C_{red}B_{ri}\rho(\omega_{ri})/2 \cong -A\mathfrak{F}C_{red} \times A_{ir}\exp(-E_{ri}/kT)/2. \quad (18)$$

Four, case 4. Assume that K'_{eq} is given by the Boltzmann population of the intermediate level as a result of a transition from either the electrode or the ion. Thus, $K'_{eq(1)} = \exp(-E_{oi}/kT)$ and $K'_{eq(2)} = \exp(-E_{ri}/kT)$, and

$$i_f = A\mathfrak{F}C_{ox}\exp(-E_{oi}/kT)\left[B_{ir}\rho(\omega_{ri}) + A_{ir}\right]$$

$$i_r = -A\mathfrak{F}C_{red}\exp(-E_{ri}/kT)\left[B_{io}\rho(\omega_{oi}) + A_{io}\right]. \quad (19)$$

(This is the case examined by Schmidt and Mark.[33]) The subscripts on the Einstein coefficients indicate the order of the transitions, e.g., A_{io} signifies the spontaneous transition from the excited intermediate level to the electrode in conformity with the reaction sequence.

The total current is given as the sum of the forward and reverse currents:

$$I = i_f + i_r. \qquad (20)$$

The equilibrium condition requires that I, the total current, be equal to zero. Applying this condition to each of the four cases yields the Nernst equation upon conversion of the energy differences to volts using $-\Delta F^\circ = n\mathfrak{F}\mathcal{E}$; for this relation the energies must be converted to kcal/mole.

If an external potential different from the equilibrium potential were applied to the electrode, the interfacial system would shift from equilibrium, as has been mentioned, and a net current would be realized. If the applied potential is small enough, it can be regarded as a perturbation. The greatest effect of this perturbation is felt through the energy terms in the exponentials.[33] The transition coefficients are assumed to remain essentially uneffected. The new energy terms appearing in the exponentials are written as $E_{mn} = E^\circ_{mn} \pm \underline{m}_{mn} \cdot \underline{E}$, where $\underline{E}$ is the applied field at the interface, and $\underline{m}_{mn}$ is the transition moment for the transition m to n.

Whether or not a charge transfer reaction is adiabatic depends upon the strength of the interaction between the reactants. If the interaction is strong between any two members of the interfacial system, it is expected that charge transfer involving that interaction will be adiabatic. If, however, within the interfacial system the association is weak between any two substituents which are involved in

the charge transfer process, then the overall charge transfer rate will exhibit a non-adiabatic character.

It is readily seen in the rates resulting from the imposition of the limits discussed in this chapter that the limits imply the character of the charge transfer. Assume, for instance, that the population of the intermediate state is non-adiabatic in one charge transfer direction, i.e., it depends on the rate of electronic transition. Once the electron reaches the intermediate state it can subsequently migrate to the final state with much greater speed; thus, it is adiabatic in the second step. Such a situation is governed by the rates (3) and (9). The overall reaction will appear non-adiabatic, and in addition, for this example one infers that the associations between the solvate and ion are much stronger than the association between the solvate and the surface. Such transfers are usually referred to as outer coordination shell transfers.

It is seen that the assumption of a detailed model for the interfacial system at an electrode leads in a simple and direct manner to the usual equilibrium Nernst equation and the expressions for the net current under the influence of an external polarization. It is apparent that if some suitable quantum mechanical description of the electrode interface, based upon the model, can be found, a priori calculations can be made leading to the electrochemical quantities of usual interest. The quantum mechanical description of the interfacial system is the subject of the next chapter.

CHAPTER III

INTERFACIAL SYSTEM: QUANTUM MECHANICAL DESCRIPTION

In Chapter II general expressions were introduced relating the rate constants, and consequently the current, of the electron transfer oxidations and reductions to the probabilities of charge transfer transitions between certain defined parts of the electrode interfacial system. It was assumed there that the transitions involved were of the spectroscopic charge transfer type--thus real transitions--and as such they may be represented in terms of Mulliken's charge transfer formalism.[33] Mulliken's treatment,[43] when applied to the electrode charge transfer process, makes use of the highest filled orbital of the metal surface atom, the lowest unfilled orbital of the solvent molecule, and the lowest unfilled orbital of the ion in its oxidized state. The choice of wavefunctions is then[33]

$$\psi_I = a\phi(el)\phi(s) + b\phi(el^+ \leftrightarrow s^-)$$

$$\psi_{II} = a'\phi(el^+ \leftrightarrow s^-) - b'\phi(el)\phi(s)$$

$$\psi_{III} = c'\phi(i^{(z+1)+} \longleftarrow s^-) - d'\phi(i^{z+})\phi(s)$$

$$\psi_{IV} = c\phi(i^{z+})\phi(s) + d\phi(i^{(z+1)+} \longleftarrow s^-). \qquad (1)$$

The basis functions for the above charge transfer functions (perturbation corrected) are $\phi(el)$, the surface state

metal wavefunction for the electrode; $\phi(s)$, the lowest unfilled molecular orbital (MO) of the solvent; $\phi(i^{(z+1)+})$ and $\phi(i^{z+})$, the crystal field orbitals of the oxidized and reduced states of the ion; and $\phi(i^{(z+1)+}\leftrightarrow s^{-})$ is the charge transfer complex wavefunction. The functions ψ_{II} and ψ_{III} are both excited state wavefunctions, the former constructed with respect to the electrode, and the latter with respect to the ion. The reason for this particular choice is seen as follows. Moving an electron from the ion or the electrode to the solvent molecule involves an expenditure of energy. The reverse movement of the electron from the solvent to the ion or the electrode results in the regaining of energy. The existence of an electron in the solvent molecule as a result of a transition from either starting point--the electrode or the ion--constitutes a metastable state. Furthermore, the continuity condition imposed by the choice of model requires that the link between the two transitions involved be through the excited state. (The charge transfer excited state is not the only possible choice. For another possibility see Chapter IV, specifically the discussion concerning the double potential well problem and its connection with the work of Halpern and Orgel.)

The wavefunctions used as basis functions in the relations (1) are perturbation corrected. The electrode wavefunctions are eigenfunctions of the Hamiltonian[33]

$$\mathcal{H} = H^{o}_{el} + V_i + V_{ads}, \tag{2}$$

where H^{o}_{el} is the Hamiltonian of the unperturbed surface state wavefunctions of the metal electrode. V_i is the electrostatic potential due to the ions at the electrode and is given by[33]

$$V_i = \sum_j (z_j e_o / r_{el,j}), \tag{3}$$

where z_j is the charge on ion j, and $r_{el,j}$ is the ion-electrode distance. Finally, the perturbation due to the adsorption of the solvent (or any other substance) on the electrode is given by V_{ads}. Likewise, the Hamiltonian for the solvent layer molecules is[33]

$$\mathcal{H} = H^{o}_{s} + V_i + V'_{el} + V_{ads}, \tag{4}$$

where H^{o}_{s} is the Hamiltonian of the free solvent molecule the eigenfunctions of which are the lowest unfilled MO's of the solvent. The effect of the electrostatic potential of the electrode is given by V'_{el} which is due only to the metal atoms on the surface of the electrode in the absence of external polarization of the electrode. Finally, the crystal field orbitals are perturbed by the electrostatic potential of the metal ions on the surface of the electrode and the Hamiltonian is[33]

$$\mathcal{H} = H^{o}_{i} + V_{el}, \tag{5}$$

where H^{o}_{i} is the Hamiltonian for the free coordinated ion.

Although the representation of the system by the simple charge transfer method given above is essentially correct (and is probably more correct the weaker the interaction), it is apparent that such a representation is at once too naive, and also too restricting. The idea of a charge transfer analogous to the spectroscopic mechanism is retained here, but it will be shown, as is expected, that the nature of the charge transfer steps is more complex than that assumed above. Hence, a more sophisticated approach is required in order that it be correctly treated.

The most logical approach to take in considering the exact nature of the transfer steps is to consider the chemical associations between species in the interface. Once some assumption has been made, and a model structure drawn to conform to the system, the next step is to determine the energy levels of the model structure. Finally, transitions are chosen between energy levels such that the transitions considered have a correspondence to physically observable transitions associated with currents.

Immediately, these investigations become that of determining the types of bonds formed between the species and their associated states in the system consisting of the metal electrode and the solvated ions. The most logical choice for beginning the description of the interfacial state is found in the existing quantum theory of chemisorption. The basic formulation of the chemisorption theory is now presented, for it yields a starting point

for further extentions particularly suited to electrode processes.

The chemisorption problem, as formulated by Koutecký,[44-48] makes use of the Koster-Slater[49,50] method developed for the treatment of impurities in metals and semiconductors. The Koster-Slater method is as follows:[51] It begins with the Schrödinger equation

$$(H^{o} + U)\psi = i\hbar(\partial\psi/\partial t), \tag{6}$$

where H^{o} is the Hamiltonian of the pure metal system. The pure metal Hamiltonian, H^{o}, has the periodicity of the lattice. U is a perturbation. The operator H^{o} with $\psi_n(\underline{k},\underline{r})$--where $\underline{k}$ is the wave vector; n, the band index; and $\underline{r}$, the space vector--gives the eigenvalue problem

$$H^{o}\psi_n(\underline{k},\underline{r}) = E_n\psi_n(\underline{k},\underline{r}), \tag{7}$$

where the $\psi_n(\underline{k},\underline{r})$ are the Bloch functions. The Bloch functions have the general property that

$$\psi_n(\underline{k},\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_n(\underline{k},\underline{r}), \tag{8}$$

where $u_n(\underline{k},\underline{r})$ has the periodicity of the crystal lattice. The Bloch functions, equation (8), can be used as a natural basis for the solution of equation (6); construct the total wavefunction

$$\psi(t) = \sum_n \int C_n(\underline{k})\,\psi_n(\underline{k},\underline{r})\,d^3\underline{k}\ . \tag{9}$$

Substituting equation (9) in equation (6) it is easily shown that the equation for the $C_n(\underline{k})$ is

$$\left[E_n(\underline{k}) - i\hbar(\partial/\partial t)\right]C_n(\underline{k}) + \sum_{n'}\int d^3k' \langle n\underline{k}|U|n'\underline{k}'\rangle C_{n'}(\underline{k}') = 0. \quad (10)$$

In equation (10)

$$\langle n\underline{k}|U|n'\underline{k}'\rangle = \int d^3r \psi_n^*(\underline{k},\underline{r})U\psi_{n'}(\underline{k}',\underline{r}). \quad (11)$$

Assuming a delta function potential of strength $V_o\Omega/(2\pi)^3$ located at the origin leads to a simple example of the Koster-Slater method. The volume of the Brillouin zone is $(2\pi)^3/\Omega$. The matrix element (11) is then

$$\langle n\underline{k}|U|n'\underline{k}'\rangle = \left[V_o\Omega/(2\pi)^3\right]\delta_{nn'}, \quad (12)$$

and is diagonal in the band index. With (12) equation (10) becomes

$$\left[E_n(\underline{k}) - E\right]C_n(\underline{k}) + V_o\Omega/(2\pi)^3\int d^3k' C_n(\underline{k}') = 0, \quad (13)$$

the solution of which is stationary in E. If $E_n(\underline{k}) - E$ is not zero, equation (13) is divided by $E_n(\underline{k}) - E$ and integrated over the Brillouin zone giving

$$\frac{V_o\Omega}{(2\pi)^3}\int d^3k \frac{1}{E_n(k) - E} = V_o\int dE' \frac{G(E')}{E' - E} = 1, \quad (14)$$

where G(E') is the density of states per volume Ω and a single spin direction.

The nature of the solutions of equation (14) is more

easily appreciated if instead of an infinite number of levels, one choses merely a discrete number N. One can then consider a function

$$f(E) = (1/N)\sum_{n} \frac{1}{E - E_n} . \tag{15}$$

The function f(E) has poles at each of the unperturbed energies, as seen in Figure 2. In between each of the unperturbed energies the function varies from $+\infty$ to $-\infty$. The poles of the function f(E) which have the value $1/V_o$ correspond to the perturbed energies. If V_o is negative, the split-off state splits off from the bottom of the energy band. If V_o is positive, the state splits off from the top of the band.

To find the energy of the split-off state it is necessary to have the $E(\underline{k})$. For the tight-binding approximation in one dimension, this is given by

$$E(\underline{k}) = E_o + 2E_1 \cos kd, \tag{16}$$

where d is the distance between atoms. E_1 corresponds to the resonance integral, and is assumed negative. From equations (14) and (16) one finds

$$\frac{V_o d}{2\pi} \int_{-\pi/d}^{\pi/d} dk \frac{1}{E_o - E + 2E_1 \cos kd} = -1. \tag{17}$$

The evaluation of the integral, and the resulting equation, gives for the energy of the split-off state

Figure 2

The determination of the energy of the split-off states by the Koster-Slater method illustrated by use of a band of six levels. (After Callaway, reference 51.)

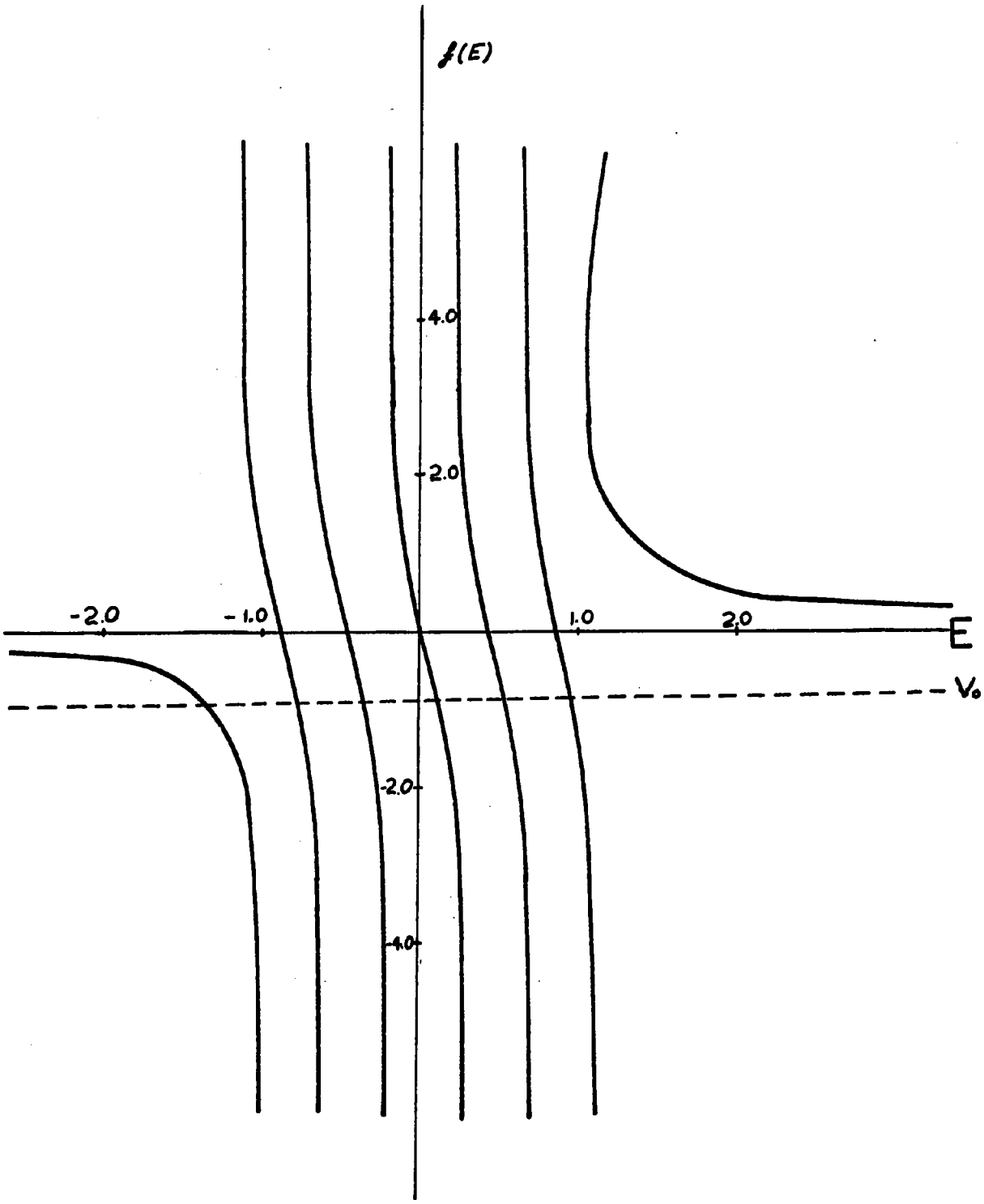


Figure 2

$$E = E_o + 2E_1\left[1 + (V_o^2/4E_1^2)\right]^{1/2}. \tag{18}$$

The solution of equation (6) can also be accomplished through use of Wannier functions. These functions are given by

$$a_n(\underline{r} - \underline{r}_\ell) = N^{-1/2}\sum_{\ell} e^{-i\underline{k}\cdot\underline{r}_\ell}\psi_n(\underline{k},\underline{r}), \tag{19}$$

where the $\psi_n(\underline{k},\underline{r})$ are the Bloch functions. (Likewise, the Bloch functions can be expanded in terms of the Wannier functions

$$\psi_n(\underline{k},\underline{r}) = N^{-1/2}\sum_{\ell} e^{i\underline{k}\cdot\underline{r}_\ell} a_n(\underline{r} - \underline{r}_\ell).) \tag{20}$$

The Wannier functions have their amplitude maxima about the lattice sites $\underline{r}_\ell$. They also satisfy the equation

$$H^o a_n(\underline{r} - \underline{r}_\ell) = \sum_m \mathcal{E}_n(\underline{r}_m - \underline{r}_\ell)a_n(\underline{r} - r_m), \tag{21}$$

where $\mathcal{E}_n(\underline{r}_m)$ is the Fourier coefficient of the energy:

$$E_n(\underline{k}) = \sum_m \mathcal{E}_n(\underline{r}_m)e^{-i\underline{k}\cdot\underline{r}_m}. \tag{22}$$

The wavefunction satisfying equation (6) is expanded as

$$\Psi = \sum_{n,\ell} A_n(\underline{r}_\ell)a_n(\underline{r} - \underline{r}_\ell), \tag{23}$$

where the A_n satisfy the equation

$$\sum_{q,n}\Big[\Big|\mathcal{E}_n(\underline{r}_p - \underline{r}_q) - i\hbar\delta_{pq}(\partial/\partial t)\Big|\delta_{nm} + U_{nm}(\underline{r}_p,\underline{r}_q)\Big] A_m(\underline{r}_q) = 0, \quad (24)$$

with the matrix element given by

$$U_{nm}(\underline{r}_p,\underline{r}_q) = \int d^3r\, a^*_n(\underline{r} - \underline{r}_p)Ua_m(\underline{r} - \underline{r}_q). \quad (25)$$

The equations (24) are called the difference equations.

For the study of the nature of the split-off state through the wavefunctions, the Wannier function representation given above is useful. H^o, as before, is the Hamiltonian operator for the pure crystal, and U is the perturbation. An analysis given by Wolff[52,53] leads directly to the expressions for the wavefunctions and the energies. Let ψ be the exact solution of the wave equation in the perturbed lattice. Then,

$$\psi = \phi_{\underline{kn}} + \frac{1}{E - H^o + is} U\psi \quad (26)$$

in the limit $s \longrightarrow +0$, and where the Bloch functions have been written as $\phi_{\underline{kn}}$. Making the assumption that the perturbation U does not mix states from different bands, the wavefunction ψ can be expanded in the Wannier functions (23). (The neglect of interband terms is not very serious if the impurity and band states arise essentially from the same atomic states.) Noting expression (20), the matrix element between ϕ and ψ is

$$\int d^3r\ \phi^*_{\underline{k}'n}(\underline{r})U\psi \;=\; N^{-1/2}\sum_{pq}\int d^3r\ a^*_n(\underline{r}-\underline{r}_p)$$

$$e^{-i\underline{k}'\cdot\underline{r}_p}\ UA_n(\underline{r}_q)a_n(\underline{r}-\underline{r}_q). \qquad (27)$$

If the perturbation U is localized at $\underline{r}_o$ and is localized such that it does not overlap appreciably with Wannier functions situated on neighboring lattice points, then a similar approximation to equation (12) can be made:

$$\int d^3r\ a^*_n(\underline{r}-\underline{r}_p)\ U\ a_n(\underline{r}-\underline{r}_q) \;=\; U_{nn}\,\delta_{op}\,\delta_{oq}. \qquad (28)$$

Now, (26) can be rewritten

$$\psi = \phi_{\underline{k}n} + \sum_{\underline{k}'}{}'\phi_{\underline{k}'n}A_n(\underline{r}_o)e^{-i\underline{k}'\cdot\underline{r}_o}$$

$$X\ \ N^{-1/2}\,\frac{U_{nn}}{E - E_{\underline{k}'n} + is}\,. \qquad (29)$$

From equation (23),

$$A_n(\underline{r}_p) \;=\; e^{i\underline{k}\cdot\underline{r}_p} + \sum_{\underline{k}'}{}'\frac{e^{i\underline{k}'\cdot(\underline{r}_p-\underline{r}_o)}}{E - E_{\underline{k}'n} + is}$$

$$X\ U_{nn}A_n(\underline{r}_o). \qquad (30)$$

For $\underline{r}_p = \underline{r}_o$ one finds

$$A_n(\underline{r}_o) \;=\; e^{i\underline{k}\cdot\underline{r}_o}\Big/\left[1 - U_{nn}\sum_{\underline{k}'}{}'(E - E_{\underline{k}'n} + is)^{-1}\right]. \qquad (31)$$

In (31) the summation can be expressed as the integral

$$(1/2\pi)^3 \int d^3k' \frac{1}{E - E_{\underline{k}'n} + is} = \int d\mathcal{E} \frac{G_n(\mathcal{E})}{E - \mathcal{E} + is}$$

$$= P\int d\mathcal{E} \frac{G_n(\mathcal{E})}{E - \mathcal{E}} - i\pi G(E), \qquad (32)$$

where P signifies the principal value. Expressing the principal value integral as $F_n(E)$, equation (31) can be written as

$$A_n(\underline{r}_o) = e^{i\underline{k}\cdot\underline{r}_o}/\left[1 - U_{nn}F_n(E) + i\pi U_{nn}G_n(E)\right]. \qquad (33)$$

Thus, the amplitude of the wavefunctions, $A_n(\underline{r}_o)$, is large at the roots E_o of the equation

$$1 - U_{nn}F_n(E_o) = 0 . \qquad (34)$$

The position of the virtual level is defined through equation (34). If the root E_o lies outside the band, $G_n(E_o) = 0$ and $A_n(\underline{r}_o) \longrightarrow \infty$, and the root represents a real bound state.

The above treatment is essentially the solution of the problem using Green's functions. For further properties of the solutions for both impurity sites and chemisorption see Appendix I.

The extension of the Koster-Slater method to the surface state[54] and chemisorption[44-48] problems is reasonably straight forward. Of prime interest here is the chemisorption problem, hence the treatment of surface states is

ignored.

For chemisorption, as with impurity sites in the infinite crystal, the success of the method is expressed through the von Laue theorem. This theorem states: At distances from the boundary of the perturbation greater than the characteristic particle wave length at the energies considered, the remaining particle density per unit energy is approximately independent of the form of the boundary. (For proof, see Appendix II.) The effect of the perturbation, to first order, is expressed in the rigid band theorem; the perturbation merely raises every energy level in the host crystal by the same amount. Energy differences between levels do not change.

The chemisorption problem is resolved by finding a prescription for the interaction, i.e., Koutecký's method.[44-48] Let the Wannier functions be the basis functions for the metal, and let the so-called equivalent orbitals be used as basis functions for the adsorbate. (Equivalent orbitals are used as they have transformation properties similar to the Wannier functions.) The Wannier functions are given by equation (19). The equivalent orbitals are constructed from molecular orbitals in much the same manner that Wannier functions are constructed from Bloch functions. In terms of Bloch functions and MO's the wave equations for the separate subsystems (R in number) are[48]

$$H^{\alpha}\psi_i^{\alpha} = E_i^{\alpha}\psi_i^{\alpha} \qquad (\alpha = 1,\ldots,R), \qquad (35)$$

where

$$H^{\alpha} = - \hbar^2/2m\nabla_{\alpha} + V_{\alpha} . \tag{36}$$

The effective potential of the selected electron in a subsystem is V^{α}. The state of the electron in the total system is given as a solution to the equation[48]

$$H\,\Theta = W\,\Theta \tag{37}$$

and

$$H = - \hbar^2/2m\nabla + V_{total}, \tag{38}$$

where

$$\Theta = \sum_{\alpha=1}^{R} \psi_i^{\alpha} . \tag{39}$$

Instead of writing the Wannier functions as (19), it is simpler to make use of the more compact notation whereby a unitary transformation is found taking Bloch functions to Wannier functions and MO's to equivalent orbitals (EO). Thus, if the Bloch functions, or the MO's are given in general by ψ_i^{α}, the generalized Wannier functions, or the equivalent orbitals are given by ϕ_r:

$$\phi_r = \sum_{i=0}^{N^{\alpha}-1} C_{ir}\psi_i^{\alpha} \tag{40}$$

with the inverse transformation given by

$$\psi_i^{\alpha} = \sum_{r=0}^{N^{\alpha}-1} C^*_{ir}\,\phi_r . \tag{41}$$

The dimension of the subsystem is given by N^{α}. The total system wavefunction can be written as

$$\Theta = \sum_{\alpha=1}^{R} \sum_{j=0}^{N^{\alpha}-1} d_j \phi_j \ . \tag{42}$$

However, instead of taking the summation over the whole subsystem, it is possible to merely take it over a limited portion of it: over $P^{\alpha} \ll N^{\alpha}$. Thus,

$$\Theta = \sum_{\alpha=1}^{R} \sum_{j=0}^{P^{\alpha}-1} d_j^{\alpha} \phi_j^{\alpha} \ . \tag{43}$$

Through the use of the variational principle, one obtains the secular equations for the coefficients d_j^{α} in (43):

$$\sum_{\beta=1}^{R} \sum_{k=1}^{P^{\alpha}-1} d_k^{\beta} P_{jk}^{\alpha\beta} = 0 \quad (\alpha = 1,\ldots,R) \ (j = 0,\ldots,N^{\alpha}-1) \tag{44}$$

where

$$P_{jk}^{\alpha\beta} = \int d\tau \ \phi^{*\alpha}_j \left[H + (V - V^{\beta}) - W \right] \phi_k^{\beta} \ . \tag{45}$$

Making use of the fact that

$$H^{\alpha}\phi_j^{\alpha} = \sum_{s=0}^{N^{\alpha}-1} \epsilon_{js}^{\alpha} \phi_s^{\alpha} = \sum_{s=0}^{N^{\alpha}-1} \sum_{r=0}^{N^{\alpha}-1} C^{*\alpha}_{rj} E_r^{\alpha} C_{rs}^{\alpha} \phi_{js}^{\alpha} \tag{46}$$

and several rearrangements similar to these used in going from (13) to (14), one finds that (44) gives

$$\sum_{k=0}^{P^{\alpha}-1} d_k^{\alpha}\delta_{ks} = \sum_{\beta=1}^{R}\sum_{i=0}^{P^{\alpha}-1}\sum_{k=0}^{P^{\beta}-1} L_{si}^{\alpha} V_{ik}^{\alpha\beta} d_k^{\beta} - \sum_{i=P}^{N^{\alpha}-1}\sum_{k=0}^{P^{\alpha}-1} L_{si}^{\alpha}\,\epsilon_{ki}^{\alpha} d_k^{\alpha} \qquad (47)$$

$$(s = 0,\ldots,N^{\alpha}-1)$$

with

$$L_{si}^{\alpha} = \sum_{p=0}^{N^{\alpha}-1} \frac{C^{*\alpha}_{pi} C^{\alpha}_{ps}}{W - E_p^{\alpha}} . \qquad (48)$$

As a result of the fact that the index k is less than P^{α}, and $\delta_{ks} = 0$ for $s \geqslant P^{\alpha}$, (47) splits into two parts

$$d_s = \sum_{\beta=1}^{R}\sum_{i=0}^{P-1}\sum_{k=0}^{P-1} L_{si}^{\alpha} V_{ik}^{\alpha\beta} d_k^{\beta} - \sum_{i=P}^{N^{\alpha}-1}\sum_{k=0}^{P^{\alpha}-1} L_{si}^{\alpha}\,\epsilon_{ki}^{\alpha} d_k^{\alpha} \qquad (49)$$

$$(s = 0,\ldots,P^{\alpha}-1)$$

and

$$0 = \sum_{\beta=1}^{R}\sum_{i=0}^{P-1}\sum_{k=0}^{P-1} L_{si}^{\alpha} V_{ik}^{\alpha\beta} d_f^{\beta} - \sum_{i=P}^{N-1}\sum_{k=0}^{P-1} L_{si}^{\alpha}\,\epsilon_{ki}^{\alpha} d_k^{\alpha}$$

$$(s = P^{\alpha},\ldots,N^{\alpha}-1). \qquad (50)$$

The condition for solubility is that the determinant vanish:

$$\left| \sum_{i=0}^{P^{\alpha}-1} L_{si}^{\alpha} V_{ik}^{\alpha\beta} - \sum_{i=P}^{N^{\alpha}-1} L_{si}^{\alpha} \epsilon_{ki}^{\alpha} \delta_{\alpha\beta} - \delta_{\alpha\beta}\delta_{sk} \right| = 0. \quad (51)$$

The roots of (51) must simultaneously satisfy (49) and (50).

The condition for the realization of localization of electrons in a region δ of the crystal is given by[46]

$$\left[d_k^{\alpha}\right]^2 / \left| \left[d_k^{\alpha}\right]^2 + \sum_{k,\beta}^{N,R-\alpha} \left[d_k^{\beta}\right]^2 \right| > \delta. \quad (52)$$

δ is some positive finite number which remains positive and finite even as N increases indefinitely. This condition was first given by Baldock[55] as a condition of the existence of a bound surface state. For the chemisorption problem, however, there are many different forms of the chemisorption bonds possible. The conditions under which they appear have been given in an extensive review by Koutecký.[56] It suffices, for purposes of this discussion, merely to iterate by name only some of the possibilities. If, for example, there are no bound electrons, it does not mean that no chemisorption bond is formed, merely that the bond is "metallic". Metallic bonds have been discussed by Grimley.[57] In the cases where there is chemisorption through localized bonding electrons Koutecký has shown that the description of these bonds follows a pattern similar to the formation of Tamm[58] or Shockley[59] surface states. Unlike the surface state problem, the chemisorption problem

shows the existence of bonding and antibonding levels, except for the metallic bonding case.[54,56] The chemisorption bonds that are localized are, in essence, split-off states either from the bottom or the top of the band from which they arise. The manner in which the chemisorption states form is strongly dependent on the changes in the resonance, exchange and overlap integrals occuring on the formation of the bonds between the sorbent and sorbate--here the metal and the sorbate.[44-48]

Of primary importance to electrode processes is the fact that a foreign substance adsorbed at the surface of a metallic crystalline material acting as an electrode is able to interact with the crystal to the extent of forming homopolar bonds. In addition, the chemisorption studies carried out by Koutecký show that not only is the formation of bonds between the surface and adsorbate described by the extended Koster-Slater method, but also the mutual interaction between adsorbed atoms.[46,48] Thus, for the adsorbed diatomic molecule, the chemisorption theory accounts,one, for the adsorption of the individual atoms to the metal surface, and,two for the formation of the bonding and antibonding states within the diatomic. The generalized chemisorption theory, as developed by Koutecký, treats the entire system; this is, of course, to be expected.

The roots of equation (51) cover the whole system. The above method, then, is the most general treatment of the problem of a molecular species interacting at the surface

of a crystal. From it, in principle, one can obtain all the necessary information. It is, however, cumbersome to use this treatment in many instances, and a simpler treatment will be developed here which gives results of particular interest to electrochemistry.

With specific reference to electrochemistry, and in particular, charge transfer, we proceed with the simplified quantum mechanical description of the system. To do this, note is made of the following properties of the electrode interfacial system. The electrode interfacial system can be broken down into three fairly distinct parts. Each part leads to the basis functions used in the final calculation. The three parts are: the infinite crystal bounded by a limiting plane--the surface, the solvate molecules, and the solvated ion. Associated with each of these separate parts are the free species Hamiltonians. (This is identical to the subsystems of the chemisorption problem considered by Koutecký.) In addition to the free species Hamiltonians there are the various perturbations occuring in the formation of the interface. These perturbations are additional to the forces responsible for the change of coordinate shell geometry. The perturbations are,one, the limiting of the infinite crystal, two, the molecular framework in juxtaposition to the surface plus the presence of the ion, and finally, three, the reciprocal surface effect on the levels of the solvated ion. Thus, it is expected that the determinant from which the energy levels of the system

will result will have the form

$$\left|\begin{array}{c|c} \text{metal terms} & |\overline{C}'| \\ \hline |\overline{C}| & \text{solvate-ion terms} \end{array}\right| = 0$$

where the $\overline{C}$ are the matrices of interaction between the two systems.

In order to have some means of examining the interfacial system and the charge transfer transitions in it, one needs to have perforce some more specific model of the system. This means, simply, that it is necessary to assume, for a particular problem, some reasonable geometry for the metal surface atoms, the solvate molecules and the ions. Calculations are then made accordingly. The methods of spectroscopic analysis relating theoretical calculation to experiment carry over here with all simplifications and all difficulties.

Two possible arrangements are presented in Figures 3 and 4. These geometries are given as examples only. There is, however, a difference between the two in the nature of the solvate orbitals used in the bonding description which is more basic and general. In Figure 3, for example, it is assumed that the solvation sphere about the ions undergoes alteration such that some nonbonding electrons of the solvate-ligand molecules originally bound to the ion are free to associate with an available site on the surface. The other conceivable arrangement,

Figure 3

The schematic representation of a possible bonding arrangement in the electrode interface. The arrangement pictured assumes an alteration of the solvate sphere of the solvated ion such that non-bonding electrons on the solvate molecules interact with the metal surface.

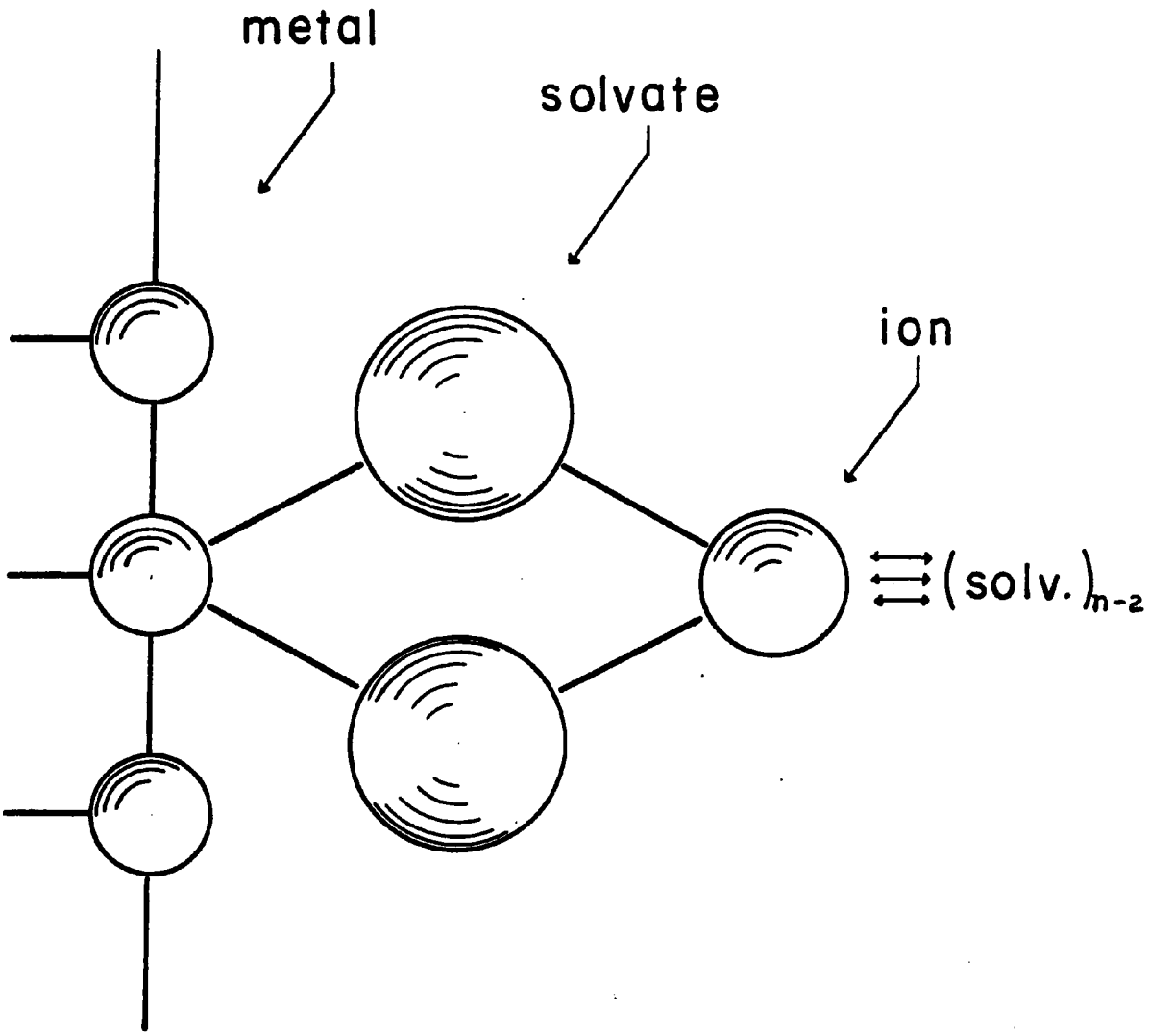
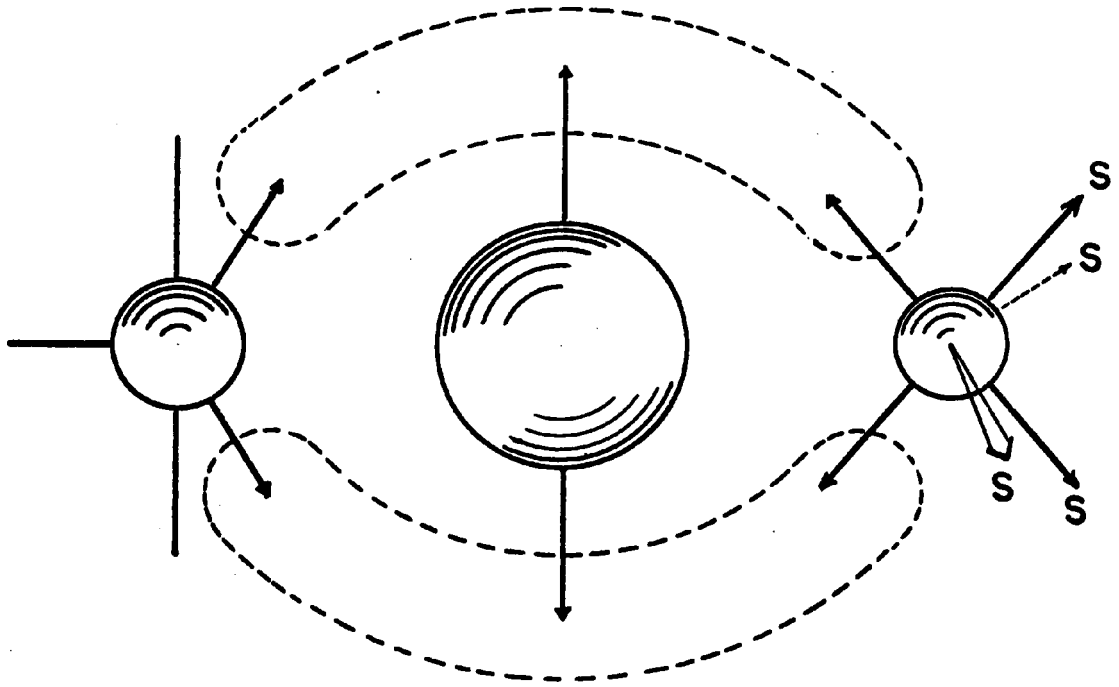


Figure 3

Figure 4

A second schematic representation of a possible bonding arrangement in the electrode interface. The arrangement pictured makes use of the assumption that common solvate electrons are shared between metal surface atom orbitals and orbitals of the ion.



metal solvate ion

Figure 4

Figure 4, has the electrons on the solvate molecule associated with both the surface and the ion in a manner "conjugating" the system composed of metal, solvate and ion. At first, it might be thought that such conjugation would have the effect of allowing free, unrestricted transfer of electrons between electrode and ion, but because of the nature of the chemisorption problem it is seen that this "degree of conjugation" does not rule out localization of electrons within certain regions of the interfacial system (see Appendix I).

The essential difference between the two figures which appears to have general implications is the fact that with one the bonding makes use of solvate orbitals situated in such a way that the bonds between metal and solvate are truly isolated from the bonds between the solvate and ion. In other words, there is an orthogonality between orbitals bonding the solvate to the metal and to the ion. With the other, the orthogonality is reduced because there are solvate orbitals associated simultaneously with both the metal surface atoms and the ions.

Quantum mechanical prescriptions abundantly exist for the determination of the energetic properties of molecules and solids. The best, of course, is one which treats the whole system in a clear physically understandable and tractable manner.[47] This would be Koutecky's method except for its intractability for complex molecular problems. The simpler description sought is a reasonable

synthesis of techniques for both solid (metal) and molecule which will lend itself to a realization of a more detailed quantum mechanical mechanism of the process of charge transfer at the interface. As all useful techniques for the calculation of molecular (and atomic) properties are approximational, it is necessary here to determine the constraints to be placed on the approximations used. In other words, to simplify the eventual computation, it is reasonable to select the parameters of greatest physical interest with the tacit implication (based mostly upon intuition) that the chosen physical parameters are at once the most important--i.e., contributing the most to the overall energy.

From the block diagram given for the determinant of the whole system it is seen that a treatment of the system can be effected by considering a synthesis of techniques existent for surface state, chemisorption and transition metal complex problems. (It will turn out, however, that the detailed treatment of the surface state is not needed, for attention will not be focused on the metal.)

An alternative method is now presented which emphasizes the solvated ions--reactants and products--and the effect upon them when incorporated into the interface. Because of the nature of the chemisorption problem, i.e., the perturbation of the sorbate on the surface does not extend very far into the metal, it is difficult to observe the effects of the perturbation through an examination

of the metal itself. However, with a smaller subsystem the perturbation effects the entire subsystem, and any measurements made on it under the influence of this perturbation reflects its presence next to the larger system. The alternative method, then, assumes the existence of a solvated ion with a geometry of the solvate about the ion identical to that found in the interface. The complete quantum mechanical treatment of the solvated ion is carried out in the absence of the interfacial surroundings. The ion, however, is imagined to retain its interfacial geometry. The imaginary removal of the ion from the interface to examine its electronic structure serves the purpose of revealing the changes affected by the ion due to its change in solvation sphere coordination geometry from the free species geometry. These energy changes are reflected in the absence of electrostatic interactions with the metal surface atoms of the electrode. Once the energy level structure has been worked out for the solvated ion in the absence of the interface, the effect of the interface is accounted for by imagining the solvated ion replaced. Electrostatic interactions are allowed to occur. In the presence of the Coulombic interactions the energy levels change and assume their final values. This imaginary process assumes, reasonably, that the Coulombic interactions can be treated as perturbations.

Assuming then that the energy level structure of the solvated ion with its equilibrium coordination sphere

geometry is known, it is necessary only to consider the effect of the electrostatic interactions. Consider first the case in which the solvated ions are merely held to the surface by chemisorptive forces; the chemisorption bonds do not play a direct role in the charge transfer process. This is the case of the solvate-metal bonds orthogonal to the solvate-ion bonds. For simplicity, assume that the solvate-ion complex has non-degenerate levels (an assumption which is weak, as most inorganic complexes have substantial degeneracy). One is interested in changes in the energy and transition moments within the solvate-ion complex due to the presence of the surface. Assuming further that lower lying levels participate in the eventual charge transfer process, the interest here will be limited to them. A situation is now constructed similar to the situation used by Murrell and Longuet-Higgins[60] for the perturbation treatment of the effect of inductive substituents on aromatics.

Denote the perturbation by H'_i. The total perturbation is the sum of the individual perturbations over the electronic index i:

$$H' = \sum_i H'_i. \qquad (53)$$

The assumption is made that it is reasonable to regard the matrix elements

$$d_r = \int d\tau_i \, \phi^*_r{}^{(i)} H'_i \phi_r^{(i)} \tag{54}$$

as being most important. Thus, with respect to equation (54) the off-diagonal matrix elements are negligible, and the matrix elements of the perturbation (53) are linear in d_r. The matrix elements can be evaluated once the $\phi_r^{(i)}$ are known.

Writing the highest bonding and lowest antibonding orbitals as ψ_{m-1}, ψ_m, ψ_{m+1}, ψ_{m+2}, etc., one can construct the state wavefunctions, $\Psi(j)$ as

$$\Gamma(j) = N^{-1/2} \sum_n (\psi_k^{-1} \psi_\ell)_n, \tag{55}$$

where the summation over n indicates the single excitations involved, and k and ℓ are the indices of the single excitations involved. The matrix elements of the perturbations H' are determined using the single excitation wavefunctions:

$$\begin{aligned} \int d\tau (\psi_\ell^{-1} \psi_m) H' (\psi_p^{-1} \psi_q) &= 0 \quad \text{for } p \neq \ell \text{ and } q \neq m \\ &= \int d\tau \, \psi_m H'_i \psi_q \quad \text{if } p = \ell,\ q \neq m \\ &= \int d\tau \, \psi_\ell H'_i \psi_p \quad \text{if } q = m,\ p \neq \ell. \end{aligned} \tag{56}$$

In addition, the relations

$$\int d\tau\,(\psi_\ell^{-1}\psi_m)H'\psi_o = 2^{1/2}\int d\tau\,\psi_\ell H'\psi_m \qquad (57)$$

and

$$\int d\tau\,(\psi_\ell^{-1}\psi_m)H'_i(\psi_\ell^{-1}\psi_m) = W' + \int d\tau\,\psi_m H'_i\psi_m - \int d\tau\,\psi_\ell H'_i\psi_\ell\,, \qquad (58)$$

where

$$W' = \int d\tau\,\psi_o H'\psi_o \qquad (59)$$

are necessary to the calculation of the matrix elements. The matrix elements between the molecular orbitals are determined by the perturbations d_r and the coefficients of the atomic orbitals of the expansion

$$\psi_\ell = \sum_r C_{\ell r}\phi_r. \qquad (60)$$

The perturbation corrected molecular orbital wavefunction is given by the familiar expression[61]

$$\psi_\ell = \psi_\ell^o + \sum_m \frac{H'_{m\ell}}{E_\ell^o - E_m^o}\psi_m^o + \text{higher order corrections.} \qquad (61)$$

To (60) and (61) there corresponds, corrected to the second order, a corrected energy

$$E'_n = H'_{nn} + \sum_m \frac{(H'_{nm})^2}{E_n^o - E_m^o} \qquad (n=1,\ldots,N). \qquad (62)$$

The energy shifts of the transition energies between levels in the solvated ionic complex are given by the differences of E'_n. When the differences are taken, the first order terms disappear, and second order terms alone remain.

The effect of the perturbation on the transition moments is seen be taking the new moment constructed from (61). This gives

$$\underline{M}'_{nk} = \underline{M}^{o}_{nk} + \sum_{m} \frac{H'_{mk}\underline{M}_{nm}}{E^{o}_{k} - E^{o}_{m}} + \sum_{m} \frac{H'_{mn}\underline{M}_{mk}}{E^{o}_{n} - E^{o}_{m}} . \qquad (63)$$

The difference between the perturbed and unperturbed transition moments merely drops the first term on the right in equation (63).

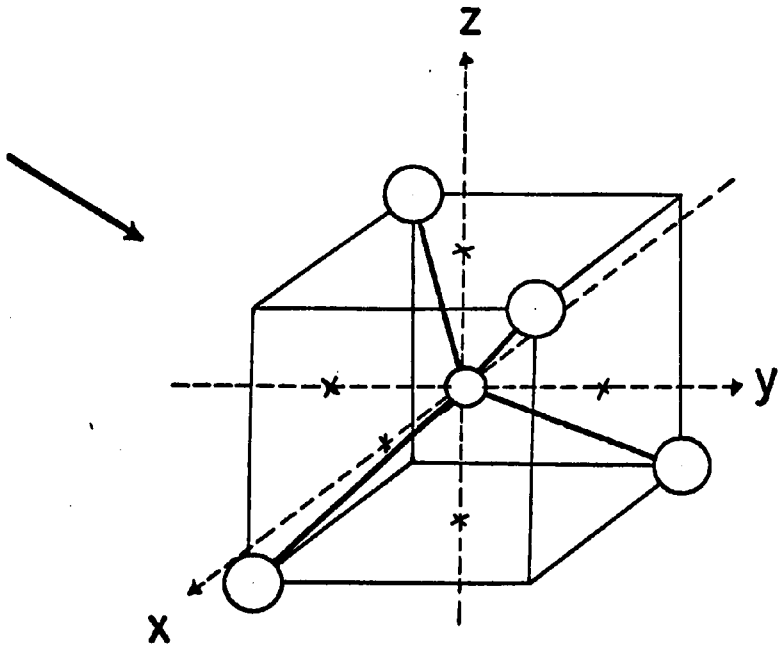
Aside from altering the pattern of degeneracies in the solvate-ion complex, the perturbation, when acting on non-degenerate levels, changes the energy as indicated. The problem of the effect of the perturbation of the degenerate levels in the system is much more difficult. The solvate-ion complex is assumed to be completely resolved in terms of the ligand field theory. When the interaction with the surface is not as strong as the interaction, or bonding, between the solvate and the ion, it appears reasonable to treat the additional effect of the surface perturbation on the degeneracies in terms of the crystal field approach. One can start with the picture of an ion surrounded by solvate of two different types: in this case the solvate itself, and the metal surface atoms (which

have a negative image charge countering the positive effective charge on the ion). The splitting of the ionic degeneracies can first be worked out in terms of a crystal field approach. A simple example serves to illustrate this point.

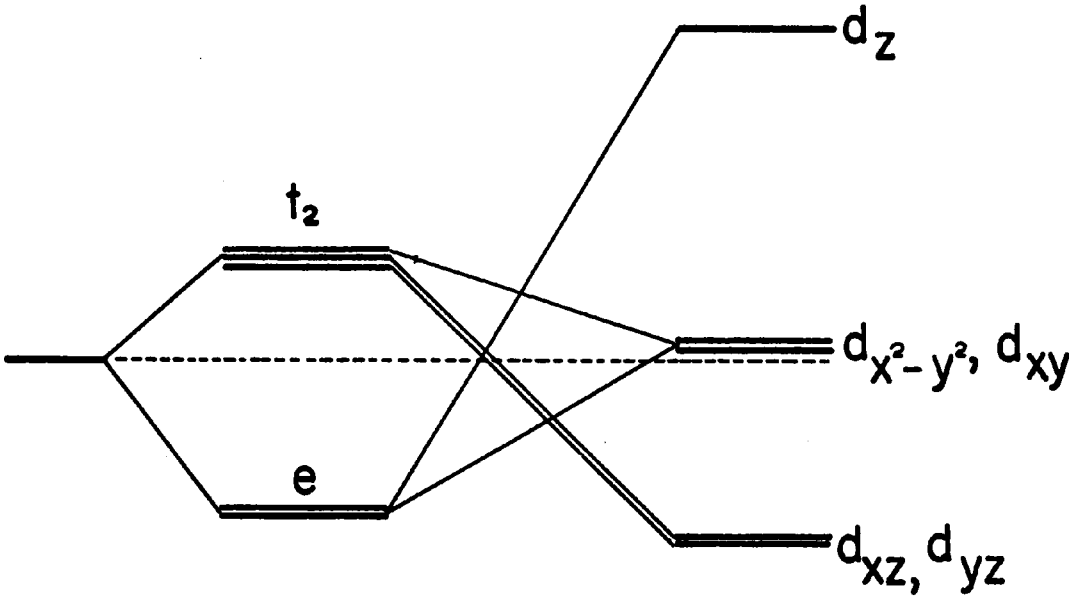
Assume that the solvated ion in its equilibrium geometry for the interfacial state is a tetrahedral complex. As usual, it is assumed that the process of adsorption has distorted the geometry of the solvate-ligand to some new geometry different from that of the bulk solution geometry, and that the energy changes accompanying the changes in coordination are reflected in the energy levels. Imagine, also, that the ion, with its interfacial geometry, can be removed from the purely electrostatic effects of the surface--as discussed above. It is then possible to determine the energy level spectrum for the pure tetrahedral complex; see Figure 5. The crystal field splitting of the degenerate d^1 levels of the transition metal ion are given in Figure 5b for the tetrahedral field. Suppose now that the solvated ion is placed back in the interfacial system with a surface metal atom situated at the point indicated by the arrow in Figure 5a. Because of the positive charge of the ion, it is expected that there is a corresponding induced negative image charge on the metal surface atom. If, as may be supposed, the three solvate molecules become displaced slightly in such a manner as to become more equitorial, the crystal field about the reactant

Figure 5

(a) The tetrahedral arrangement of ligands about a central metal ion in a cubic symmetry group. (b) The splitting of the degenerate d^1 levels in a tetrahedral field, and in a trigonal bipyramidal field. The tetrahedral splitting is pictured on the left and the trigonal bipyramidal splitting on the right.



(a)



(b)

Figure 5

ion becomes more that of a trigonal bipyramid. For this virtual bipyramid it is assumed that the polar axes are longer than the equatorial. The perturbation potential for such a situation is given by[62]

$$V' = A'' + B''_1(z^2 - r^2/3) + B''_2(x^2 + y^2 - 2r^2/3) + C''(x^2r^2 + y^2r^2 - r^4/5) + D''_1(35z^4 - 30z^2r^2 + 3r^4) + D''_2(x^4 + y^4 + 2x^2y^2), \quad (64)$$

where $A'' = -Z(3/a + 2/b)$; $B''_1 = -3Z/b^3$; $B''_2 = -9Z/4a^3$; $C'' = -42Z/8a^5$; $D''_1 = -Z/4b^5$; and $D''_2 = -315Z/64a^5$. The a and b are the equatorial and polar axes.

The first term in the expression (64), A", merely raises all the energy levels in a uniform manner. The quadratic terms cause the splitting given in Figure 5b on the right.

As a result of the fact that the model assumes an interfacial geometry different from that of the bulk of the solution, one expects, in this example, to find evidence experimentally of a tetrahedral complex. This would be expected for some spectroscopic technique. As is by now obvious, this will not be the case. The additional splitting caused by the negative image charge on the electrode has acted to make the solvated ionic complex behave, as far as d-level transitions are concerned, as if it were a trigonal bipyramid.

In this example, it is assumed that the charges on the

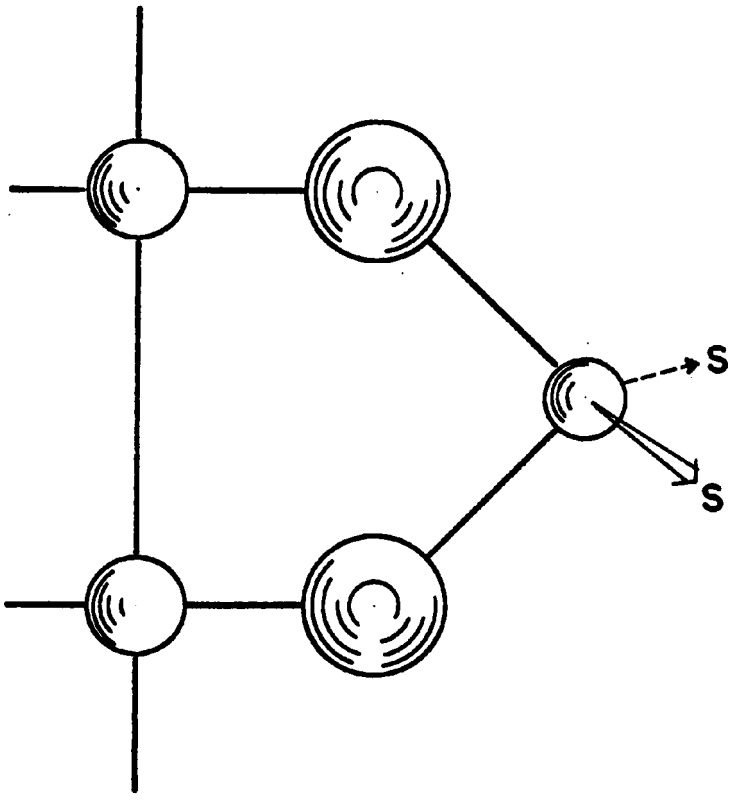
polar molecules, i.e., the surface atom and one of the molecules of solvation, are equal. Furthermore, it is assumed that the polar distances on either side of the ion are the same. This is, of course, an exaggeration of reality but if the image charge is not too large on the surface, it will probably not be too much greater than the induced polarization charge in the molecule at the other end of the pole. The splitting presented for the trigonal bipyramidal field in Figure 5b is the extreme case. The actual splitting will probably lie somewhere in between the tetrahedral and trigonal bipyramidal field extremes.

If, on the other hand, the solvated ionic complex is associated with the electrode surface atoms through an arrangement pictured in Figure 6, then one would expect little additional lifting of degeneracy in the central ion.

For the case at hand, that of the so-called orthogonal orbitals, it is assumed that the charge transfer transitions take place between non-bonding orbitals of the metal surface atoms, and some relatively low excited state of the solvate-ion complex. For purposes of discussion, it is further assumed that all changes in the solvate-ion complex energy levels are known, including the lifting of degeneracies, as a result of placing the reactant ions in the interface. Furthermore, all states of the solvated ion are characterized as to which electrons from the electrode will be excited. Not yet characterized are the surface orbitals

Figure 6

A possible arrangement of solvate molecules in the interface between the metal surface and the reactant ion which does not significantly alter the existing degeneracy on the central ion.



metal solvate ion

Figure 6

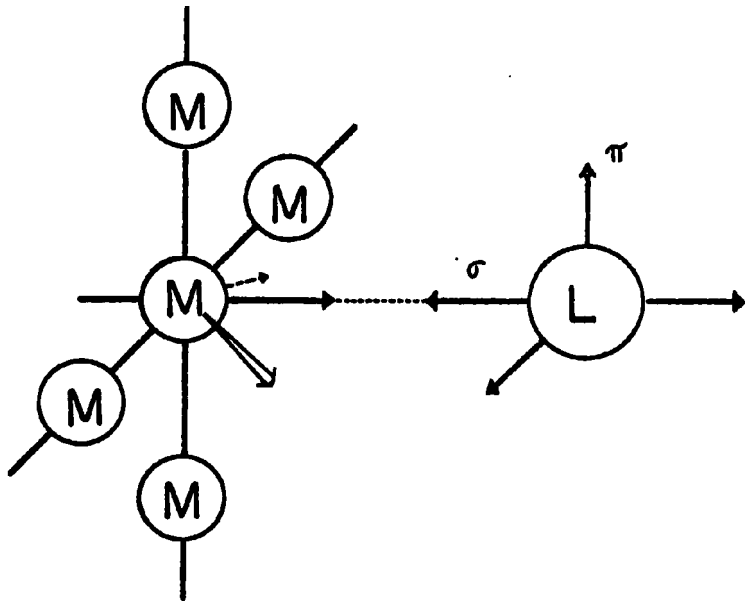
of the electrode from which the electrons will be promoted. The effect of the adsorbed solvate-ionic species on the orbitals of the surface is dependent on which surface plane the species are adsorbed. Another qualitative discussion serves to illustrate the factors involved.

Consider a simple cubic system. Choosing a metal atom of the surface it is seen that it is surrounded by four nearest neighbors. For the cubic system the symmetry element is D_{4h}. The surrounding four nearest neighbors cause a splitting of the d levels in the transition metal atom identical to the crystal field splitting in a tetragonal field. If the surface of the metal is chosen as the x,y-plane with the z axis normal to the surface and directed outward, the splitting is as shown in Figure 7. The predicted splitting leaves only the d_{z^2} and the degenerate pair d_{xz} and d_{yz} available for bonding at the surface. It is presumed that the electron responsible for the charge transfer comes from one of these orbitals which when combined with the solvated ion remains nonbonding, or becomes antibonding.

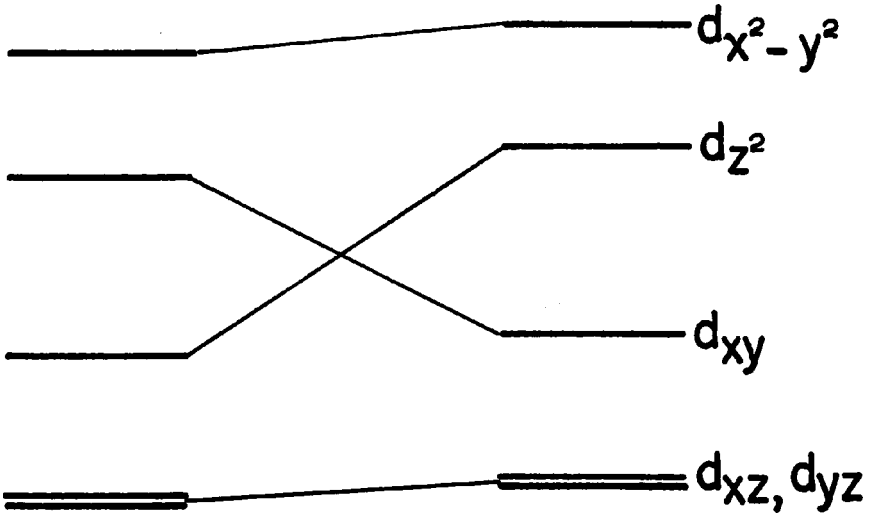
Assume an example configuration--Figure 3. Furthermore, assume that there is occupancy of the d_{z^2} nonbonding orbitals such that charge transfer transitions can arise from them. The interaction of the solvated ion with the d_{xz} or d_{yz} will, of course, alter their energy levels. The antibonding levels arising from the d_{xz} or d_{yz} may also be occupied, and charge transfer transitions

Figure 7

The splitting caused by a D_{4h} field about a central transition metal atom. The presence of an additional ligand along the z-axis induces a change from the square planar field to the tetragonally distorted field.



D_{4h} crystal field



square planar

tetragonal distortion

Figure 7

from them to the solvated ionic levels are possible.

It is desirable to consider the effect on the surface levels when the interface is formed. In terms of the Hamiltonian the effect can be written as a perturbation by the solvated ion on the surface:

$$H_1 = H_o + V_{eff}\,, \tag{65}$$

where H_o is the Hamiltonian for the metal including the surface atoms, i.e., H_o accounts for the existence of surface states where they exist. The perturbation, V_{eff}, due to the effective charge seen by the metal surface, can be approximated in terms of the ligand field relation giving the fractional positive charge on the central coordinated metal ion modified to give the fractional charge seen by the metal surface:[63]

$$(1/n) \sum_i \frac{1 + \lambda_i G_i}{1 + 2\lambda_i G_i + \lambda_i^2} = Z_{eff}, \tag{66}$$

where λ_i is defined by the MO

$$\psi_i = N(\psi_M + \lambda_i \phi_{lig}). \tag{67}$$

The coordination number is n and G_i is the overlap integral of the metal ion with the linear combination of ligand (solvate) orbitals. The effective potential at the surface is

$$V_{eff} = - Z_{eff}\, e_o^2/R, \tag{68}$$

where R is the distance between the metal surface and the ion. It is readily seen that the effective charge, if positive, has the effect of lowering the energy of the nonbonding orbitals. With respect to these nonbonding orbitals the antibonding orbitals formed from the d_{xz} or d_{yz} will be of higher energy. If they are occupied, it is probable that the expected charge transfer transitions will arise from these antibonding orbitals unless symmetry restrictions on the transition moments prohibit them. One expects that the energy of the charge transfer transition is given by the usual expression[64]

$$E_{ct} = \emptyset - EA + C,$$

where $\emptyset$ is the work function of the bare metal, and EA is the electron affinity of the solvate-ion complex. The factor C takes into account all the interfacial electrostatic and adsorptive effects which change the individual levels in accord with the above discussions.

Consider now the effect of allowing for conjugation between the metal system and the solvated ions. (In a sense, this model corresponds to the consideration of a limited exciton model.) The bonding involved is given by the example in Figure 4. Let the changes in the molecular orbitals be determined entirely by the value of the resonance integral:[65]

$$\beta_{uv} = \int d\tau \emptyset^*_u(i) H_i^{core} \emptyset_v(i). \qquad (70)$$

This is analogous to the assumption made by Pople[66] for the case of unsaturated hydrocarbons. The treatment, then, can follow that given by Longuet-Higgins and Murrell[65] whereby at first changes in H_i^{core} are ignored as the system condenses and are brought in later as perturbations. First examined are the effects of condensing the system into the interfacial state upon the state wavefunctions, and upon the individual singly excited levels. As a matter of convenience, introduce the metallic state wavefunctions

$$\Omega(q) = N^{-1/2} \sum_{m}^{M} (\phi_f^{-1}\phi_g)_m \qquad (71)$$

for the excited states in analogy to (55). Now, assume the following for the wavefunctions of the system: One, for an excited state, the mixing of singly excited levels is assumed complete before condensation of the system; two, there are singly excited configurations of the forms $\psi_k^{-1}\psi_l$, $\phi_f^{-1}\phi_g$, and the charge transfer configuration $\psi_k^{-1}\phi_g$.

The electronic repulsion between two singly excited configurations is given by the integral[65]

$$\int(\psi_a^{-1}\psi_b)H(\psi_c^{-1}\psi_d)d\tau = 2\iint\psi_a(i)\psi_b(i) \times (1/r_{ij})\psi_c(j)\psi_d(j)d\tau_i d\tau_j$$

$$-\iint\psi_a(i)\psi_c(i)(1/r_{ij})\psi_b(j)\psi_d(j)d\tau_i d\tau_j \,, \qquad (72)$$

H is the total Hamiltonian for the system with $\beta_{uv} = 0$. The locally excited levels $\psi_a^{-1}\psi_b$ and $\psi_c^{-1}\psi_d$ interact, and the interaction is given by the first term on the right of (72). The interaction of this type is a form of electron correlation. If the singly excited levels in the second integral represent configurations in which electrons are transferred in the same direction, the first integral is zero. For a zero resonance integral there will be no mixing of singly excited configurations in which the electrons are transferred in opposite directions. It is assumed, as in the Longuet-Higgins and Murrell treatment,[65] that for the case of the zero resonance integral, charge transfer transitions can be ignored. Such charge transfer transitions become allowed when the resonance integral is non-zero. These interactions, for the zero resonance integral, will mix states $\Gamma(j)$ and $\Omega(q)$, but not the singly excited configurations through charge transfer.

The allowance now for the existence of a non-zero resonance integral introduces the effects of conjugation. The resonance integral, β_{uv}, has the effect of mixing together configurations which differ in the position of one electron. The formulae, given by Longuet-Higgins and Murrell,[65] are

$$\int \psi_o H^{core} \psi_a^{-1} \psi_b d\tau = 2^{1/2} \int \psi_a(i) H_i^{core} \psi_b(i) d\tau_i \qquad (73)$$

where ψ_o is the ground state wavefunction, and

$$\int \psi_c^{-1} \psi_a H^{core} \psi_c^{-1} \psi_b d\tau = \int \psi_a(i) H_i^{core} \psi_b(i) d\tau_i \quad (74)$$

$$\int \psi_a^{-1} \psi_c H^{core} \psi_b^{-1} \psi_c d\tau = -\int \psi_a(i) H_i^{core} \psi_b d\tau_i . \quad (75)$$

Now, mix the locally excited configurations on the segments, i.e., the metal and the solvated ionic systems, according to the symmetry regulations one has linear combinations of the form $(1/2)^{1/2}(\psi_1^{-1}\psi_2 \pm \phi_1^{-1}\phi_2)$ with energies $E \pm R$, where E is the energy of the local transition, and R, the electronic repulsion integral. For each linear combination there will be as many E as there are locally excited configurations mixed. In addition to the locally excited configurations, the non-zero resonance integral mixes into the overall state charge transfer transitions. The energy of the electron transfer configuration is given by[65,67]

$$\int \psi_1^{-1} \phi_2 H \psi_1^{-1} \phi_2 d\tau = E_2 - E_1 - \iint \psi_1(i) \psi_1(i) \times (1/r_{ij}) \phi_2(j) \phi_2(j) d\tau_i d\tau_j . \quad (76)$$

With the expressions (73) to (76) and the linear combinations of locally excited configurations, it is possible to perform the perturbation calculation-- the resonance integrals are the perturbations--and observe the effects through the shifted energy levels. The locally excited

configurations now have mixed into them some charge transfer character.

As far as the charge transfer step itself is concerned, the most important expression is (76). However, once the electron is transferred to the ionic system, it is in a locally excited state of that system until it makes the final transition to the ground state of the reduced ion-solvate complex. In the type of bonding considered, the effect of allowing for conjugation, in addition to the effect of electronic repulsion due to the surface atomic system, alters the energy level scheme of the complex. Thus, one does not expect the locally excited transitions in the complex to be the same as those one might calculate considering the complex free.

The conclusion of chemisorption theory is that the effect of the perturbation on the surface does not extend to any great depth into the metal system. Hence, it is assumed that if the metal crystallographic surface of interest is known, then it is a relatively simple matter to determine the locally excited configurations of the surface system which interact in the above treatment. If the association of the solvated ionic complex with the surface is not great, the effect of allowing for conjugation may be simply to mix charge transfer configurations into the locally excited configurations of the complex. This simplifies the problem considerably, since now one has only to deal with the solvated ionic system. The charge

transfer from the electrode metal surface, being accounted for by the work function of the metal in a manner given by expression (69) where here C takes into account the effect of the complex on the Fermi level, includes the electronic repulsion terms.

It has been seen in this chapter how it is possible to consider the effects of the metal surface on the energy level system of the solvated ionic complex. Such a treatment accounts in a physically meaningful manner for the effects of condensation of the individual subsystems into an electrode interfacial state. As the process of condensation will be reflected most in the solvate-ion complex, it has been assumed reasonable to concentrate on it.

CHAPTER IV

CHARGE AND ENERGY TRANSFER MECHANISMS

In Chapter II the general model of the interfacial system was developed. The model was constructed on the basis of an equilibrium system existing in the electrode interface. Quite simply this means that one has chosen the assumption that chemical rates are far greater than electronic rates. Being so, the electronic rates govern the current while the system remains under an equilibrium situation, and possibly even near it. Such a model is readily seen to be analogous to the model chosen by Halpern and Orgel[68] to investigate homogeneous charge transfer through a bridged intermediate. In this work, a bridged intermediate is also assumed through the interaction of the solvate layer adsorbed to the electrode, and sandwiched between the electrode and the reactant ions.

It was seen in Chapter II that there were two electronic transitions responsible for the current. One takes the electron from the electrode surface atom to an intermediate level, and the other takes the electron from the reduced ion to the intermediate level. Once an electron is in the intermediate level, it can relax to a lower energy state either through electronic or electronic-vibrational relaxation. The current, then, is dependent upon either the energy absorption, of energy emission process. It turns out that the rate of energy transfer which results in

electronic transitions is the rate of oxidation or reduction, and thus the current.

It is of interest to consider the current of what might be a typical reaction to see what may be inferred about the transition probability. Considering that the typical reaction has an activation energy of one-half an electron volt, and at normal temperatures gives an exchange current of several milliamps, then the following is concluded, based on the assumption of a relation of the form

$$i_e = i_e^o \exp(-E_a/kT). \qquad (1)$$

Inserting the values mentioned, it is found that i_e^o is of the order of 20 amps. Thus, although the current is small relative to i_e^o as a result of the high activation energy with respect to $T = 300^oK$, it may be possible that the transition(s) involved are highly allowed. However, taking into consideration the fact that i_e^o depends on the Faraday constant and the concentration, it appears that the transition(s) and their associated probabilities are of the class normally referred to as forbidden. Anticipating the results to be found in Chapter VI, it is probably a good guess to say that a classification of electrode reactions based on an oscillator strength analogy may be of immense value in categorizing reactions. It remains now to be seen in what manner energy can be transferred to the system to effect the transitions responsible for

the current.

Whereas in the previous chapters electronic aspects have been emphasized and other factors only tacitly acknowledged--for example, vibrational factors--it is apparent that there is a strong mutual action of both electronic and vibrational factors on the rates of electron exchange. In Chapter II, general rate conditions were expressed, and general limits between individual rate constants examined. These were then subsequently shown to lead to current expressions under the assumption of a general oscillatory field perturbation and the further assumption of the low temperature approximation. The low temperature approximation implies, in the case of electrode processes, electronic transitions effected by energies higher than the usual system phonon energies. Energies of these magnitudes are necessary for populating the intermediate level. If the energy absorption process is rate determining, then obviously it is necessary to consider sources of energy which fit the prescription. If, however, relaxation from an excited state is rate determining, then it is possible that vibrational factors may play a very large role.

Having the general kinetic relations developed in Chapter II, it is necessary here to place some additional assumptions into the model of the system to arrive at the means of explicitly evaluating the rate constants. The essential feature distinguishing the model assumed for the electrode interface is the assumption, for most cases, of

localization of metal electrons in a chemisorption bond, or for weaker interactions localization of the electron in a surface state. Thus, within a finite distance into the metal from the metal surface itself, the surface and its adsorbed layer--the solvated ions--may be considered an entity, i.e., a surface complex. With this form of the surface complex, electron exchange leading to electrochemical reactions is considered solely within the framework of the surface complex. This allows considerable simplification conceptually of the nature of the charge transfer. Of course, the system is not entirely isolated from the rest of the metal. Once a reduction is accomplished, for example, a volume electron can be donated to the metal surface atom. It is assumed, however, that this exchange follows much faster than the initial transition taking the electron from the ground state--essentially localized on the metal surface atom--to the final state localized on the ion. It is important to bear in mind the fact that the delineation of the system into an essentially localized surface complex is made mainly to facilitate the focusing of one's attention on particular interactions effecting the transfer. Thus,it is contended that the electron transfer is rate-determining only within the surface complex; to effect these transfers energy must be exchanged to and from the surface complex with the remainder of the total electrode system. To a very large degree, the consideration of the mode of charge transfer becomes similar to that of

the transfer between two unlike ions in free solution. It will be seen that the above considerations are well justified, as the surface of the metal, with whatever is attached to it, acts as a scattering impurity to a sea of electrons (not necessarily the Fermi sea).

Within the above description considerable freedom is allowed for the choice of particular arrangements of the reactants. Reactant configurations of most interest are those which involve the simultaneous interaction of orbitals of the solvate molecules with the surface atoms and the ions. In effect, the presence of these molecules, and the dependence of the charge transfer upon them (assumed, of course) gives a description analogous to that for the transfer between certain ions in solution (c.f. Taube and others[8]). The difference here is that the electronic initial and final states are not degenerate.

The evaluation of the rates, and hence the transition probabilities, is a problem of time-dependent perturbation theory. Depending on the nature of the perturbation, the evaluation can proceed along several different lines. It is intended here to present a brief review of the time-dependent perturbation theory formalism. This will give the basic rules for the transition probabilities which subsequently can be examined in detail for specific model mechanisms. The perturbations can be stationary or time-dependent. The dipole-dipole interaction giving the well known van der Waal's forces is an example of a station-

ary perturbation. General multipole interactions intermolecularly give rise to a means of energy transfer. Fluctuating charge distributions, with their associated fields, give rise to time-dependent perturbations. The presence of a barrier, which is a self perturbation of the system, can lead to transitions through consideration of the development in time of the non-stationary states of the overall system.

Considering first the stationary perturbation one is lead to the transition probability per unit time as follows.[69]

The time-dependent wave equation is

$$\mathcal{H}\psi = -\hbar/i\partial\Psi/\partial t, \tag{2}$$

where the Hamiltonian $\mathcal{H}$ is given by

$$\mathcal{H} = H^{\circ} + H'. \tag{3}$$

The well known solution of this problem is accomplished through the use of the variation of coefficients technique. The solution is obtained by constructing the wavefunction satisfying (2) from unperturbed wavefunctions of H°. Thus,

$$\psi = \sum_{n} c_n(t)\phi(q)\exp(-iE_n t/\hbar). \tag{4}$$

The $c_n(t)$ terms depend upon time. From the first order perturbation one arrives at an expression for the coefficients $c_k^{(1)}(t)$:

$$c_k^{(1)}(t) = -\frac{H'_{km}}{\hbar}\,\frac{e^{i\omega_{km}t} - 1}{\omega_{km}}. \tag{5}$$

In equation (5) the matrix element connecting states k and m is H'_{km}. The probability that the system will be found in the state k at time t is given by

$$\left|c_k^{(1)}(t)\right|^2 = \frac{4\left|H'_{km}\right|^2 \sin^2(1/2\,\omega_{km}t)}{\hbar^2\omega_{km}^2}, \tag{6}$$

where $\omega_{km} = (E_m - E_k)/\hbar$. Considering a transition to a group of final states whose energy range is small compared to $\hbar\omega_{km}$, one gets an expression for the transition probability per unit time:

$$w(t) = t^{-1}\sum_k \left|c_k^{(1)}(t)\right|^2 = t^{-1}\int dE_k \left|c_k^{(1)}(t)\right|^2 \rho(k) \tag{7}$$

where $\rho(k)$ is the density of final states. Inserting (6) into (7) and performing the indicated integration yields the Fermi golden rule:

$$w(t)/t = w = \frac{2\pi}{\hbar}\rho(k)\left|H'_{km}\right|^2. \tag{8}$$

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For a harmonic perturbation, the treatment is similar. Take the perturbation to be

$$H'(t) = H' \sin \omega t', \tag{9}$$

then the first order amplitudes, $c_k^{(1)}(t)$, are

$$c_k^{(1)}(t) = -(H'_{km}/2i\hbar)\left[\frac{e^{i(\omega_{km}+\omega)t}-1}{\omega_{km}+\omega} - \frac{e^{i(\omega_{km}-\omega)t}-1}{\omega_{km}-\omega}\right]. \qquad (10)$$

The squared modulus of the coefficients leads to two expressions, one for each resonance condition; the resonance conditions are $E_k = E_m \pm \hbar\omega$. One resonance condition, $E_m + \hbar\omega$, corresponds to an absorption, while the other corresponds to an emission--induced emission. Each expression for the squared modulus of the coefficients yields the Fermi golden rule.

A somewhat different way of looking at the problem is to examine the nonstationary state wavefunctions and to determine the probability that a state n is occupied at a time t.[70,71] This problem is well known for the degenerate double potential well.[72,73] Robinson and Frosch have examined the treatment for a non-degenerate double potential well in relation to a study of the mode of radiationless energy transfer. As shall now be shown, this approach is useful in expressing the exchange of charge at an electrode in terms of an analogy to the treatment used by Halpern and Orgel.[68] The method is quite general, and leads eventually to essentially the same results as obtained by direct application of the Fermi rule.

The total Hamiltonian, $H_o + H'$, contains all terms of the system plus surroundings.[72] Any term so large as

not to be experimentally detected through the time factors is included in H_o.[72] The total Hamiltonian contains terms in the system modified by the surroundings. Making use of a stationary perturbation the degenerate problem is worked as follows:[71,72] At time $t = 0$ the two degenerate wavefunctions $\phi_1(x)$ and $\phi_2(x)$ are combined into the linear combinations

$$\psi_1 = (1/2)^{-1/2}[\phi_1(x) + \phi_2(x)]$$
$$\psi_2 = (1/2)^{-1/2}[\phi_1(x) - \phi_2(x)] \qquad (11)$$

by the time-dependent perturbation H'. $\phi_1(x,t)$ and $\phi_2(x,t)$ are then developed in time in the usual manner: in terms of ψ_1 and ψ_2, with the time factors $\exp(\pm iE't/h)$. ψ_1 and ψ_2 are the stationary state wavefunctions. Making use of the initial conditions (11) the modulus, $\phi_1^*(x,t)\phi_1(x,t)$ is

$$\phi_1^*(x,t)\phi_1(x,t) = \phi_1(x)^2\cos^2 2\pi H'_{12}t/h + \phi_2(x)^2\sin^2 2\pi H'_{12}t/h. \qquad (12)$$

The probability that the state signified by ϕ_2 is occupied is given by the time-dependent coefficients

$$c^*_2 c_2 = \sin^2 2\pi H'_{12}t/h. \qquad (13)$$

The electron makes transitions back and forth between the two potential wells with a frequency of $2H'_{12}/h$.

If there is an energy difference between states 1 and

2, then the results are those given by Robinson and Frosch.[72] The combinations

$$\psi_1(x) = a\phi_1(x) + b\phi_2(x)$$

$$\psi_2(x) = b\phi_1(x) - a\phi_2(x) \qquad (14)$$

are made. Using a procedure similar to that used above for the degenerate case the probability that $\phi_2(x)$ is occupied is given by[71,72]

$$c^*_2 c_2 = 4H'^2_{12}/(4H'^2_{12} + \Delta E^2)\sin^2 1/2(4H'^2_{12} + \Delta E^2)^{\frac{1}{2}} t/\hbar, \qquad (15)$$

where $\Delta E < E_1, E_2$. For states close to resonance, i.e., $H'_{12} \approx E$

$$c^*_2 c_2 = (2\pi H'_{12} t/h)^2, \qquad (16)$$

while for states far from resonance, i.e., $H'_{12} \ll E$,

$$c^*_2 c_2 = (4H'^2_{12}/\Delta E^2)\sin^2 1/2(\Delta E t/\hbar). \qquad (17)$$

It has been pointed out by Robinson and Frosch[72] that when the time is $t \ll \hbar/H'_{12}$, and with a very large number of final states, contributions to the probability of leaving $\phi_1(x)$ are greater for $\Delta E \gg H'_{12}$ than for $\Delta E \approx H'_{12}$.

Expression (17) above is of interest in connection with the electron transfer from, for example, the electrode atom to an ion through a bridge intermediate. With equation (17) it is possible to effect a treatment analogous to that of Halpern and Orgel in the following manner. The matrix

elements can be written in a form similar to[68]

$$H'_{12} = \frac{H_{12} - S_{12}H_{11}}{(1 - S_{12}^2)}, \tag{18}$$

where

$$H_{11} = \langle \phi_1 | H | \phi_1 \rangle, \quad H_{12} = \langle \phi_1 | H | \phi_2 \rangle, \quad \text{and } S_{12} = \langle \phi_1 | \phi_2 \rangle .$$

One can consider, in analogy with Halpern and Orgel, that the electron transfer takes place through the interaction of filled electronic levels of the bridging group. Wavefunctions

$$\phi_1 = (1/N!)^{1/2} |\phi_A \phi_X \overline{\phi}_X|$$

$$\phi_2 = (1/N!)^{1/2} |\phi_B \phi_X \overline{\phi}_X| \tag{19}$$

can be written, where N is a normalizing factor. Evaluating the specific matrix elements leads, as Halpern and Orgel have shown, to

$$H_{11} = \langle \phi_A(1)\phi_X(2)\phi_X(3) | H | \phi_A(1)\phi_X(2)\phi_X(3) \rangle - \langle \phi_A(1)\phi_X(2)\phi_X(3) | H | \phi_X(1)\phi_A(2)\phi_X(3) \rangle \tag{20}$$

and

$$H_{12} = \langle \phi_A(1)\phi_X(2)\phi_X(3) | H | \phi_B(1)\phi_X(2)\phi_X(3) \rangle - \langle \phi_A(1)\phi_X(2)\phi_X(3) | H | \phi_X(1)\phi_B(2)\phi_X(3) \rangle . \tag{21}$$

The first term in (21) has been pointed out to suggest a direct exchange between A and B, while the second seems to

indicate the double exchange A to X and X to B.[68]

Unexplored by Halpern and Orgel, however, was the possibility of exchange involving unfilled levels on the bridging group. The consequences of this assumption are now indicated. Assuming that the unfilled levels participate, it is possible to write initial and final state wavefunctions as

$$\begin{aligned} \phi_1 &= |\phi_A| + |\phi_X| \\ \phi_2 &= |\phi_B| + |\phi_X|, \end{aligned} \tag{22}$$

(the individual wavefunctions are expressed in their determinantal form to include the possibility that these individual wavefunctions may be molecular orbitals, or other more complicated functions of the various substituents), ignoring the normalization factors. It is quite readily seen that the matrix elements assume the form

$$H_{11} = \langle\phi_A|H|\phi_A\rangle + \langle\phi_X|H|\phi_X\rangle + 2\langle\phi_A|H|\phi_X\rangle \tag{23}$$

$$H_{12} = \langle\phi_A|H|\phi_B\rangle + \langle\phi_A|H|\phi_X\rangle + \langle\phi_B|H|\phi_X\rangle + \langle\phi_X|H|\phi_X\rangle. \tag{24}$$

Again in (24) it is seen that one term suggests a direct exchange, and the other terms indicate the indirect stepwise transfer. It is noted that the wavefunctions (22) can be thought of as composed of a ground state term in ϕ_A or ϕ_B with the admixture of an excited state term of the overall system; to wit, configuration interaction.

In conformity with molecular quantum mechanics, the degree to which the direct exchange term effects the overall transition matrix is related to the direct overlap term between A and B. If, as has been assumed in general in this work, the overlap between A and B (in other words, between the surface atom of the electrode and the ion) is small, then that term will be of vanishing importance, and indeed will be ignored. The major part of the electron transfer is accounted for by the indirect exchange terms in expression (24), and also in expression(21) if that is the route the electron takes.

The deficiencies in this type of approach appear to be twofold. The first, and most serious, has to do with the fact that this approach fails to take direct cognizance of the effect of the surroundings upon the rate of transition. It is the very coupling with the outside that tells the nature of the specific form of the matrix element leading to the transition. Ultimately, in any treatment, it is of interest to know the exact form of the perturbation elements--or, where this is impossible, at least an approximate form. Were, for example, the interaction with the surroundings to be of the dipole-dipole type, the matrix element within the surface complex would be of the dipole type itself.

Furthermore, if the interaction with the surroundings is, say, dipole-dipole, the total transition probability is a product of the individual transition dipoles. Thus,

one acts as a weighting factor upon the other. We assume the important transition moment is that within the surface complex, the one leading to the current. It is, however, inaccurate to say that the other transition moment yields unit probability, for in many cases it may not. In most cases where the transition moment in the sensitizer molecules--either the metal or molecules in the surroundings-- does not yield unit probability, it is obvious that what happens in the surroundings effects the surface complex transition moment by reducing the overall probability of energy exchange. Thus, coupling with the surroundings can play an important part in the magnitude of the current observed.

The second deficiency is concerned with the approach taken in the assumption that the electron transfer is effected through use of filled orbitals of the bridging group. Accepting any legitimate bonding scheme as applicable to this problem, i.e., charge transfer formalism, molecular orbital methods, or the ligand field approach, it is seen that the ground state description, or configuration, is one in which electrons are associated with bonding orbitals of lower energy with respect to the initial and final states. To effect a transfer, then, an electron must be promoted from a bonding orbital of the bridge group and ion, say, to a final state configuration with the electron localized more about the ion. This must occur before an electron from the initial state localized primarily

about the surface metal atom can "fall" into the recently vacated orbital between the bridge group and the ion. This is, of course, a simplification in that many minor transitions would probably have to take place within the bridging group once an electron has been "promoted out" of its system. Such a mechanism using such transitions is said to involve virtual transitions. If one asserts, as has been done in this work, that the electron exchange transitions involve real transitions within the system, then a description of the Halpern-Orgel type places heavy reliance upon an expected long lifetime of the first excitation mentioned, i.e., that from the bridge group-ion bonding orbital to an ionic orbital assumed an excited state. Credence is lent to the mechanism because many of the transitions are Laporte forbidden. The question remains, however, of just how much credence is to be attached to this mechanism.

The other mechanism proposed here, utilizing the higher energy unfilled levels of the system, has the virtue of a long overall lifetime by reason of the two possible directions in which the electron can migrate once it has attained the excited configuration: to the initial or final state. Conversely, the intermediate configuration can be populated either from the electrode or the ion. The lifetime of the excited state is

$$\tau = 1/(A_{io} + A_{ir}), \qquad (25)$$

with the spontaneous emission coefficients which were given in Chapter II. It is expected that the individual lifetimes will be fairly long since the possibility is great that the individual transitions leading to the intermediate excited configuration from either the surface atoms of the electrode or the ion will also be Laporte forbidden. Thus, attention will continue to be focused only on mechanisms which are envisioned to make use of unfilled levels of the bridging solvate system.

Of most interest are the specific mechanisms for energy and charge transfer. The first mechanism to be considered regards the fluctuating lattice system of the interface and the solution--as much as it can be regarded as a lattice--as the source of an oscillatory field quantity.[33] As Gouterman[74] has done, it is possible to initiate a treatment of the relaxation from the excited intermediate state in an analogy to the semiclassical treatment of radiation. Assume the perturbation

$$H'_{int} = \sum \eta_\alpha x_\alpha F_x \cos(\omega t + \underline{K}\cdot\underline{r}_\alpha), \qquad (26)$$

where η_α is the coupling constant with the phonon field, x_α is the displacement of the particle α, F_x is the force analogous to $e\underline{E}$ in the electric case, and the cosine term gives the interaction in terms of a phonon plane wave polarized along the unit vector $\hat{i}$. The relation between ω and K is given by $\omega = c_s K$, where c_s is the velocity of sound in the medium. The total Hamiltonian is now

$$H = H_o + H'_{int}, \tag{27}$$

where H_o is the total Hamiltonian for the free molecule. Using the semiclassical treatment of radiation, Gouterman[74] gives the probability of the excitation to a state m from a state n as

$$c_m^* c_m = F_x^2 \sin^2 1/2(\omega_{mn} - \omega)t/\hbar^2(\omega_{mn} - \omega)^2$$

$$X \left| \int dx \psi_m^* \sum_\alpha \eta_\alpha x_\alpha \exp(-i\underline{K}.\underline{r}_\alpha) \psi_n \right|^2, \tag{28}$$

$\omega_{mn} = \omega_m - \omega_n$. The energy density of the phonon field is given by $F_x^2/4\pi$, and in analogy to the photon case one can write

$$F_x^2 \longrightarrow 1/3(8\pi)2/3 . e^2 \int d\omega \, \rho_s(\omega), \tag{29}$$

where the factor 2/3 arises due to the longitudinally polarized phonons and e^2 is inserted to make the units work out correctly. The Einstein coefficient B_{mn} is found to be

$$B_{mn} = (4\pi^2/3\hbar^2)2/3 \left| \underline{\mu}_{mn}^s \right|^2, \tag{30}$$

where $\underline{\mu}_{mn}^s$ is given by

$$\underline{\mu}_{mn}^s = e \int dx \psi_m^* \left[\sum_\alpha \underline{r}_\alpha \exp(-\underline{K}.\underline{r}_\alpha) \psi_n \right]. \tag{31}$$

The analogy to the Planck formula for the energy density of a phonon field is found in the Debye theory for the determination of the specific heat, and is given by

$$\rho_s(\omega) = 3/2(\hbar\omega^3/\pi^2 c_s^3)\left[\exp(\hbar\omega/kT) - 1\right]^{-1}$$

$$\text{for } \omega < \omega_{max} \qquad (32)$$

and

$$\rho_s(\omega) = 0 \qquad \text{for } \omega > \omega_{max}, \qquad (33)$$

where ω_{max} is the cutoff frequency for phonon radiation. The number of states making the transition from m to n (where $E_m < E_n$) is equal to the number of states making the reverse transition at equilibrium and

$$N_n\left[B_{nm}\rho_s(\omega) + A_{nm}\right] = N_m B_{mn}\rho_s(\omega). \qquad (34)$$

From the Boltzmann distribution law

$$N_n/N_m = \exp(-\hbar\omega/kT) \qquad (35)$$

and from equation (34) one finds

$$\rho_s(\omega) = A_{nm}/B_{nm}\left[\exp(\hbar\omega/kT) - 1\right]^{-1}. \qquad (36)$$

From equations (30), (32) and (36) the Einstein spontaneous emission coefficient is

$$\begin{aligned} A_{nm} &= 3/2(\hbar\omega^3/\pi^2 c_s^3)B_{nm} && \text{for } \omega < \omega_{max} \\ &= (4\omega^3/3\hbar c_s^3)\left|\underline{\mu}_{mn}^{s}\right|^2 \\ &= 0 && \text{for } \omega > \omega_{max}. \end{aligned} \qquad (37)$$

Substituting the values of the Einstein coefficients, (30)

and (37), into the expressions for the currents, equations II(19), one finds

$$i_f = C_{ox} A \mathcal{F} (4\omega_{ri}^3/3\hbar c_s^3) \left| \underline{\mu}_{ri}^s \right|^2 \exp(-E_{oi}/kT) \times \left(\left[\exp(E_{ri}^s/kT) - 1 \right]^{-1} + 1 \right)$$

$$i_r = - C_{red} A \mathcal{F} (4\omega_{oi}^3/3\hbar c_s^3) \left| \underline{\mu}_{oi}^s \right|^2 \exp(-E_{ri}/kT) \times \left(\left[\exp(E_{oi}^s/kT) - 1 \right]^{-1} + 1 \right). \qquad (38)$$

The ω and E^s in (38) are to be distinguished from the other energies E, as they are phonon energies, while the others are activation energies of much greater magnitude. If the phonon energies are much less than the energies of transition between levels, then making use of the high temperature approximation for phonons, and ignoring energy differences between phonon modes and activation energies, one gets for (38)[75]

$$i_f = C_{ox} A \mathcal{F} (4\omega_{ri}^2/3\hbar^2 c_s^3)(kT) \left| \underline{\mu}_{ri}^s \right|^2 \exp(-E_{oi}/kT)$$

$$i_r = - C_{red} A \mathcal{F} (4\omega_{oi}^2/3\hbar^2 c_s^3)(kT) \left| \underline{\mu}_{oi}^s \right|^2 \times \exp(-E_{ri}/kT), \qquad (39)$$

where the high temperature approximation is

$$\left[\exp(\hbar\omega/kT) - 1 \right]^{-1} \cong kT/\hbar\omega. \qquad (40)$$

The phonon mechanism presented above represents a means of transferring electronic excitation energy to lattice

vibrations. It presumes that once the relaxation process has begun, the process is irreversible, and that the system will continue to relax to a ground state situation. If the process is irreversible, then only the first step, i.e., the transfer of the first quantum to a phonon mode, is rate-determining.

The treatment of Gouterman's[74] transfers excitation energy to lattice modes. On the other hand, taking equations II(6) and II(12),

$$k_{rate} = K'_{eq(1)} k_3 = \exp(-E_{oi}/kT)\, k_3 \qquad \text{II(6)}$$

and

$$k_{rate} = K'_{eq(2)} k_2 = \exp(-E_{ri}/kT)\, k_2, \qquad \text{II(12)}$$

we want to evaluate the relaxation rate constants k_2 and k_3 for conversion of excitation energy to the following: one, the irreversible transfer of the electronic energy to another molecule, and, two, the relaxation of the excited state by conversion of the excitation energy to vibrational energy in the same molecule. In the first case, the energy is transferred to another molecule which then can relax vibrationally, or electronically and possibly luminesce. To investigate these modes of energy transfer leading to relaxation, use is made of the approach taken by Robinson and Frosch[73] (hereafter referred to as RF). Using the RF approach enables one to examine the effect of strong and weak coupling, in the limit of states

in near resonance, on the total transition probability. This treatment makes more evident the nature of the dependence of the transition probability on the Franck-Condon overlap integrals.

Assume with Robinson and Frosch[73] that there is a set of vibrational levels of the final electronic state which, if the surface complex could be considered free, would be in near resonance with the initial state. The final states are coupled directly to the initial state, as they have pointed out. The interaction matrix elements are written as H'_n and are derived from the electronic matrix element H'_{el} when the vibrational factors are known. Assume further that the environment, other than the environmental factors originally responsible for the interfacial state, has no further effect on the electronic matrix element H'_{el}. Taking the environment into account alters the total matrix element only through the Franck-Condon factors.[73]

In spite of the strong association between the surface atom and the rest of the metal, the remainder of the coupling in the system is weak. This is so for the simple reason that the couplings of importance, the couplings between the surface atom and the solvated ion, are weak. Energy has to be transferred to effect a transition by an electron from the surface atom to the solvate system and the ion. If, on the other hand, one considers energy dissipation as rate-determining, then the conversion of large units of molecular energy in one step processes is

assumed not to take place. This comes about from the necessity of keeping the Franck-Condon factors at a reasonable magnitude. Thus, one can expect that the dissipation process will involve incremental losses of energy in such a manner that the relation given by RF holds[73]

$$\sum_r v_r \nu_r = \Delta E/h, \tag{41}$$

where v_r is the quantum number of the ith normal mode having a frequency ν_r. It is asserted that the high energy modes associated with geometry changes of the molecule and local environment are most important (RF). The inclusion of the environment leads to additional final states nearly degenerate with one of the directly coupled final states. It is assumed (RF) that there are (N - 1) of these zero-order states coupled throughout by a matrix element α. There are then N final states with a band width of approximately α.

The mathematical limits given by RF for the radiationless transition processes of interest are applicable to this work. They are $\Delta E \gg H''_n \gg \alpha$ and $\Delta E \gg \alpha \gg H'_n$. The former limit means that the vibrational relaxation time determines the overall relaxation rate, or the rate of energy transfer. The latter limit, the limit of most interest, indicates that the electronic lifetime is greater than the vibrational lifetime, and that it is the electronic matrix element for the directly coupled final states which is rate-determining.

Consider the condition (RF) where energy states are not too far, yet not too close to resonance and thus contribute the most to the transition probability. This allows the use of equation (17). For the limit $\Delta E \gg \alpha \gg H'_n$, irreversibility is built into the transition probability since the consideration of normalization giving $N^{-1/2}H'_n$ yields an extremely small probability of the return to the initial state compared to α.[72]

The total transition probability is given by the integration over indirectly coupled final states followed by summation over the directly coupled final states.[72] Thus,

$$w_n(t) \approx \int_{-\alpha/2}^{\alpha/2} \frac{4H'^2_n}{N(\Delta E)^2} \rho(\Delta E) \sin^2 \frac{\Delta E t}{\hbar} \, d\Delta E. \qquad (42)$$

Here one expects $\rho(\Delta E) \sim N/\alpha$. Integration gives directly

$$w_n(t)/t = (2\pi H'^2_n/\alpha\hbar). \qquad (43)$$

The total transtion probability is then

$$W(t)/t = (2\pi/\alpha\hbar) \sum_n H'^2_n = (2\pi H'^2_{el}/\alpha\hbar) \times \sum_n \langle \phi''_n | \phi'_o \rangle^2, \qquad (44)$$

where $\langle \phi''_n | \phi'_o \rangle$ is the Franck-Condon integral.

In the theory of radiationless transitions as put forward by Robinson and Frosch, there are two limits of of physical interest.[73] These have already been mentioned

and are $\Delta E \gg H'_n \gg \alpha$ and $\Delta E \gg \alpha \gg H'_n$. It is of most interest to examine the meaning these limits have with respect to the rate constants for the electron transfers. It is possible, and in fact probable, that one limit applies to one transition, while the other applies to the second. If one assumes the vibrational relaxation time is rate-determining, i.e., the first limit, then there will be many electronic transitions between the initial and final states corresponding to many transfers of energy to and from the surface complex. As α is the indirect coupling matrix, and if the second transition is rate-determining--meaning the relaxation--it is seen that the first limit compared to the relaxation through the second transition yields only a steady state population of intermediate. This conclusion is based on the assumption that $H'_n(2)$--meaning here the second transition, while $H'_n(1)$ refers to the first--is less than α, and hence rate-determining. If, however, the first limit is assumed for both transitions, the direction of the reaction will be determined by the relative weight of the two vibrational factors. Alternatively, if the intermediate directly couples the initial state with the final, then the rate of overall transfer can be expected to be rate-determining.

With the assumption of an equilibrium situation in the interface it is expected that the second limit, for the most part, will be the only limit of importance. For departures from equilibrium, the first limit is expected to assume the

most importance. This is so simply because the first limit gives the vibrational factors and structural changes as rate-determining. Thus, assuming the second limit, the RF inter- and intramolecular rates are given by[73]

$$w(t)/t = (2/\hbar^2)\tau_{vib}\left[\langle\phi'_a\phi_a|\phi'_b\phi_b\rangle\right]^2 H'^2_{el}, \qquad (45)$$

where $\psi'_a\psi_b \rightarrow \psi_a\psi'_b$ (ψ' represents the excited vibronic state), and

$$w(t)/t = (2/\hbar^2)\tau_{vib}\langle\phi'_a|\phi_a\rangle^2 H'^2_{el}, \qquad (46)$$

where $\psi_a' \longrightarrow \psi_a$. In (45) $H'_{el} = \langle\theta'_a\theta_b|H'|\theta_a\theta'_b\rangle$ and the θ are the electronic wavefunctions. In (46), $H'_{el} = \langle\theta'_a|H|\theta_a\rangle$. Furthermore, in (46) ψ' refers to the excited electronic state in its zeroth vibrational state. Energy is transferred to a higher vibrational state of energy ΔE. The intermolecular rate given by equation (45) refers particularly to the transfer of energy from the excited species to some other molecular system, while the originally excited species relaxes without change of geometry. Change of geometry implies breakdown of the interfacial system. Rates dependent on geometry changes presumably would not become important until the system has been perturbed some distance from the equilibrium state.

One readily sees that for the case in which the relaxation from an excited intermediate state is rate controlling the transition probabilities (45) and (46) can be identified

with the rate constant; they must yet be summed over all the directly coupled final states.

Still unexamined in detail is the case of a current governed by the absorption of energy by the surface complex. It is very unlikely that an excited state of reasonable magnitude (from $\frac{1}{2}$ ev. to about 5 ev.) can be obtained through any conversion of vibrational to electronic energy in a one step process. There is, however, a population of states in the surroundings (i.e., the surroundings being that part of the total system neighboring the interface) with excitation energy sufficient to be transferred to the surface complex. It is clear that the applicable limit for the energy exchange is again the second limit: $\Delta E \gg \alpha \gg H'_n$. Actually, it cannot be clearly stated that the vibrational factors alone are responsible for the irreversibility. It is possible that there is a secondary electronic transition which is sufficiently rapid compared to the initial transition, so that the initial transition is rate-determining.

As the second limit applies to absorption processes, the equation (45) applies. However, now ϕ'_a and θ'_a are excited vibrational and electronic wavefunctions of the surrounding subsystems, and not the surface complex!

It has been asserted that the perturbation Hamiltonian is to be found in the total Hamiltonian for the total system. It is clear from the discussion in Chapter III that the perturbations appearing in the total Hamiltonian leading to

transitions are not one in number. There are, in fact, many possible perturbations within the system. Thus, it is clear that the perturbation H' appearing in the matrix element H'_{el} is a sum of individual perturbations. Depending upon the importance of a single perturbation to the energy transfer process, it will either be rate-determining, or it can be ignored. A qualitative estimate of the importance of a perturbation, realized through its matrix element, is made by examining each element in terms of the applicable limit. Presuming the second limit, and presuming that all $H'_n \ll \alpha$, the question reduces to one of comparing the H'_n with ΔE. For resonance interactions the limit is $\Delta E \ll H'_n$. Obviously, the greater H'_n is with respect to ΔE, the closer that particular energy transfer mechanism is to a resonant transfer. Consequently, the more important it will then be. The greater a particular H'_n, the greater is the association in that particular direction. In other words, a reflection of H'_n is found in the orbital overlap, and the greater a particular overlap between two or more segments of the interfacial system as opposed to the others, the greater will be the energy transfer utilizing that "bond".

If there is strong association between the metal and the solvated ionic systems in the interface, then it is easy to see that energy will be preferentially transferred to and from the metal to the surface complex. Of greatest interest, as far as energy transfer from the metal is

concerned, is the transfer leading to transition rates dependent upon energy absorption in the surface complex (as opposed to relaxation processes).

Of the possible mechanisms of coupling and transferring energy between the metal interior and the surface, one of the best suited makes use of the interaction arising from electron-electron correlation. Intermolecularly, electron-electron correlation gives rise to the van der Waal's forces. Intramolecularly--including metals as "molecules"--a lowering of the ground state energy is observed. This intramolecular ground state energy lowering is brought about as a result of the mixing of excited state energies by the application of second-order perturbation theory. Such effects have been shown by Simpson[76] for linear unsaturated carbon molecules. Similarly, energy lowering is found in metals by identical reasoning. It is known, however, that the application of perturbation theory to the electron correlation in the electron gas of a metal leads to logarithmic divergences which come about by the long range effect of the potential.[77] That divergences are not expected in this treatment is the result of the use of the dielectric response analysis of Nozières and Pines.[78,79]

If in a metallic system there appears a charge density in a restricted region of the metal, the remaining metallic conduction electrons will move to screen the foreign charge.[77] If the foreign charge density fluctuates, the screening charge density also will fluctuate. The move-

ment of electrons in the Fermi sea to screen a test charge yields a dielectric response to that charge. Thus, the test charge shows the correlation of the electronic motion through the response of the free electron sea.

In making use of the dielectric response analysis it will be necessary to consider interband transitions as the principal contributors. This is so because of the fact that most transitions of interest in the surface complex are greater than the energy of any intraband transition. First, however, a review of the dielectric response analysis will be given.

Current solid state theory makes extensive use of the field theoretic concept of second quantization. As it will be used here, a short résumé of the formulation of the Hamiltonian is given in Appendix III. The Hamiltonian in terms of density fluctuation operators is[53,77]

$$H = 1/2m \sum_j p_j^2 + \sum_{k\neq 0} \frac{2\pi e^2}{k^2} (\rho_k^+ \rho_k - n), \qquad (47)$$

where ρ_k^+ and ρ_k are the density fluctuation operators defined in Appendix III. The first term above gives the kinetic energy, and the second, the electrostatic, interelectronic interaction. The above Hamiltonian (47) is the unperturbed Hamiltonian of the metallic system. The next step in the process of dielectric response analysis is to examine the effect on the metallic system of a test charge. This test charge is external, and assumed weak.

If the external charge density is signified by $z\rho_{ext}(r,t)$, it is easily found that the Fourier transform of the Poisson equation is [53,77]

$$i\underline{k}.\underline{D}(\underline{k},\omega) = 4\pi z\,\rho_{ext}(\underline{k},\omega) \tag{48}$$

and

$$i\underline{k}.\underline{E}(\underline{k},\omega) = 4\pi\left[-e\langle\rho(\underline{k},\omega)\rangle + z\,\rho_{ext}(\underline{k},\omega)\right], \tag{49}$$

where $\langle\rho(\underline{k},\omega)\rangle$ is the Fourier coefficient of the induced charge density in the metal brought about by the presence of the external charge. Dividing equation (48) by (49) and using $\underline{D}(\underline{k},\omega) = \varepsilon(\underline{k},\omega)\underline{E}(\underline{k},\omega)$ gives

$$1/\varepsilon(\underline{k},\omega) = 1 + e\langle\rho(\underline{k},\omega)\rangle/z\,\rho_{ext}(\underline{k},\omega). \tag{50}$$

$\varepsilon(\underline{k},\omega)$ is the time dependent Fourier coefficient of the dielectric constant. The constant is a direct measure of the reduction in the strength of the potential of the external test charge. It is, hence, a measure of the effectiveness of the screening of the external charge by the conduction electrons. In order to evaluate $1/\varepsilon(\underline{k},\omega)$, it is necessary to evaluate $\langle\rho(\underline{k},\omega)\rangle$. The evaluation can be carried out through use of time-dependent perturbation theory. [53,77] Write for the total Hamiltonian

$$H = H_o + H_{int}, \tag{51}$$

where H_o is given by equation (47) and H_{int} is specified through the external test charge $z\,\rho_{ext}(\underline{r},t)$. The interaction is switched on adiabatically, thus one can write

$$H_{int} = - \lim_{\delta \to 0} \sum_k \frac{4\pi ez}{k^2} \rho_k^+ \rho_{ext}(\underline{k},\omega)\, e^{-i\omega t} e^{\delta t}. \quad (52)$$

Writing the total Schrödinger equation

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = (H_o + H_{int})\Psi(t), \quad (53)$$

the wavefunction $\Psi(t)$ can be expanded in terms of the many-body eigenstates where

$$H_o \Psi_n = E_n \Psi_n \quad (54)$$

and

$$\Psi(t) = \sum_n \Psi_n\, a_n(t) e^{-iE_n t/\hbar}. \quad (55)$$

Proceeding in the usual manner one finds

$$a_n(t) = \frac{4\pi ez}{\hbar k^2} \left(\frac{\rho_{ext}(\underline{k},\omega)(\rho_k^+)_{no} e^{-i(\omega - \omega_{no} + i\delta)t}}{\omega + \omega_{no} - i\delta} \right.$$

$$\left. - \frac{\rho_{ext}^+(\underline{k},\omega)(\rho_k)_{no} e^{i(\omega + \omega_{no} - i\delta)t}}{\omega + \omega_{no} - i\delta} \right). \quad (56)$$

Retaining linear terms in $a_n(t)$ only, one calculates the expectation value of ρ_k.

$$\rho_k(t) = \sum_n \langle 0|\rho_k|n\rangle a_n(t)e^{-i\omega_{no}t} + \langle n|\rho_k|0\rangle a_n^+(t)e^{i\omega_{no}t} \quad (57)$$

and direct substitution leads to

$$\rho_k(t) = -\frac{4\pi ez}{\hbar k^2}\rho_{ext}(\underline{k},\omega)e^{-i(\omega + i\delta)t} \times \left\{\sum_n \frac{|(\rho_k^+)_{no}|^2}{\omega - \omega_{no} + i\delta} - \frac{|(\rho_k)_{no}|^2}{\omega + \omega_{no} + i\delta}\right\}. \quad (58)$$

Use is made of the fact that

$$\langle\rho_k(t)\rangle = \langle\rho(\underline{k},\omega)\rangle e^{-i\omega t} \quad (59)$$

to finally get the result

$$1/\varepsilon(\underline{k},\omega) = 1 + \frac{4\pi ez}{\hbar k^2}\sum_n |(\rho_k^+)_{no}|^2 \times \left(\frac{1}{\omega - \omega_{no} + i\delta} - \frac{1}{\omega + \omega_{no} + i\delta}\right). \quad (60)$$

The real and imaginary parts of equation (60) can be separated out by making use of the relation

$$1/(x - a + i\delta) = PP\ 1/(x - a) - i\pi\delta(x - a), \quad (61)$$

where PP = principal part. They are

$$\mathrm{Re}\frac{1}{\varepsilon(\underline{k},\omega)} = 1 + \frac{4\pi e^2}{\hbar k^2} \sum_n \left| (\rho_k^+)_{no} \right|^2 \times \left(\frac{2\omega_{no}}{\omega^2 - \omega_{no}^2} \right) \tag{62}$$

and

$$\mathrm{Im}\frac{1}{\varepsilon(\underline{k},\omega)} = -\frac{4\pi^2 e^2}{\hbar k^2} \sum_n \left| (\rho_k^+)_{no} \right|^2 \times \left[\delta(\omega - \omega_{no}) - \delta(\omega + \omega_{no}) \right] . \tag{63}$$

We now have the requisite expressions with which to discuss the nature of the interactions. It is noted in anticipation of results to be obtained that expression (63) is of a form similar to the "golden rule" for the time-dependent transition probability.

Consider now the effect of a time-independent potential arising from the charge density $z\rho_{ext}(\underline{r},0)$.[53] This charge density corresponds to the presence in the metal of a point impurity which is stationary. The potential for such a charge distribution can be written immediately

$$\phi_{imp}(r) = \sum_k \frac{4\pi ze}{k^2 \varepsilon(\underline{k},0)} e^{i\underline{k}\cdot\underline{r}} \tag{64}$$

in terms of its Fourier expansion. The static dielectric constant is given by $\varepsilon(\underline{k},0)$. Using this potential,

(64), one finds that the screening charge is[53]

$$\Delta = z\left(\frac{1}{\varepsilon(0,0)} - 1\right). \qquad (65)$$

The screening of the charge impurity introduced at the surface is considered a ground state phenomenon. In other words, the alteration of the bare metal electronic disposition caused by the introduction of some new structure at the surface creates a change in the metal electronic system. With respect to the ground state description of all interacting members, i.e., the metal and the surface, the screening effect on the unexcited surface complex is regarded as contributing to the ground state. If either the metal interior system or the surface complex becomes electronically excited, then this is regarded as a time-dependent "test charge" interacting with the ground state system. With the foregoing in mind, it is possible to make the following distinction concerning the nature of the interactions between the metal and the surface complex.

The metal is considered in its ground state description, and the surface complex in an excited state description. It is immediately apparent that it is possible for the excited surface complex system to lose energy to the body of the metal. Considering the converse, the surface complex in its ground state and an electron of the metal system in an excited state, it is seen that the metal system can transfer its excitation energy to the surface. It is reasonable to expect that the same energy levels are used

for the respective subsystems in the description of the energy transfer no matter which direction the energy is transferred. With this in mind, the expression obtained for the transition in one direction should be similar to that obtained for the reverse transition. As the perturbation is oscillatory, there are in fact two expressions obtained for the transition probability. One is for the absorption, and the other for the induced emission. Thus, taking

$$1/(x + a + i\delta) = PP\ 1/(x + a) - i\pi\delta(x + a)$$

instead of (61) the absorption expression ensues.

The best description of the interaction between the metal and the surface complex is given by (52). That equation (52) is a weak interaction does not preclude its use here, as the interaction energies involved will be at most of the order of a few electron volts. These magnitudes are much less than the energies involved in the fast electron interactions, i.e., around 10 to 12 ev. Define now the interaction of a charge density[53,77,78]

$$e\,\rho_{ext}\,(e^{-i(\omega t + \underline{k}.\underline{r})} + e^{i(\omega t - \underline{k}.\underline{r})}). \qquad (67)$$

This charge density leads to the interaction (52) plus its complex conjugate. Physically, we are interested in the interaction of the metal with the oscillating dipole moment of the transition involved in the surface complex. It is essential, then, that there be an expression for the

transition probability which contains an explicit representation of that dipole moment, or at least its Fourier coefficient.

Given a medium containing permanent dipoles, it is known from the theory of electricity that a polarization charge density can be defined as

$$e\,\rho_{ext} = \underline{\nabla}.\underline{P}, \tag{68}$$

where $\underline{P}$ is the polarization vector, or dipole moment per unit volume. If a unit volume is assumed, then one can write

$$\underline{P} = \underline{\mu}_{mn}, \tag{69}$$

where $\underline{\mu}_{mn}$ is the transition dipole moment associated with the transition from a state m to a state n, and it is assumed that this dipole results in the polarization charge density. In order to have a substitute for the Fourier transform of the external charge density, ρ_{ext}, it is necessary to seek a transform of (69) through (68). It has been assumed that the polarization charge density is indeed the external charge density. Express the fact that the charge density and the dipole moment can be developed in a Fourier series:

$$\rho(r) = \sum_{k} \rho(k)\, e^{-i\underline{k}.\underline{r}}, \tag{70}$$

and

$$\underline{\mu}(r) = \sum_{k} \underline{\mu}(k)\, e^{-i\underline{k}\cdot\underline{r}}. \qquad (71)$$

From expressions (68), (70) and (71) it follows that

$$e\,\rho_{ext}(k) = -\,ik\,\mu(k). \qquad (72)$$

The interaction part of the Hamiltonian is now written

$$H_{int} = \frac{4\pi e}{k}\, i\,\mu_b(k)\,\rho_k^{+}\, e^{-i\omega t + \delta t} + c.c. \qquad (73)$$

Following the treatment used before for the charge density, retain the factors to the first order in $\mu_b(k)\, e^{-i\omega t}$ (where the index b signifies the bands involved in the transition, and k is the usual wave vector). By the usual methods of time-dependent perturbation theory involving an oscillatory perturbation, it is immediately found that

$$w(k,\omega) = (2\pi/\hbar^2)(4\pi e/k)^2 \left|\mu_b(k)\right|^2 \sum_{n} \left|(\rho_k)_{no}\right|^2 \times \delta(\omega + \omega_{no}), \qquad (74)$$

and this is the desired result. The angular frequency is the angular transition frequency in the surface complex.

The expression for the transition probability (74) can be rewritten in terms of the imaginary part of the reciprocal dielectric coefficient. Comparing expressions (74), (66) and (60) leads to

$$w(k,\omega) = -\,(8\pi/\hbar)\left|\mu_b(k)\right|^2 \mathrm{Im}\left[1/\varepsilon(\underline{k},\omega)\right]. \qquad (75)$$

Thus, knowledge of the dielectric response of the metal along with knowledge of the transition moment of the surface complex reveals the character of the transitions between the metal and the solvate.

The discussion has not yet given consideration to the effect of the metal on the transitions between the solvate and the ions. It is expected that the effectiveness of the metal is reduced with respect to initiating transitions between the solvate and the ions due to the greater separation of this portion of the surface complex from the metal interior. Added to this separation is the additional factor of an effective dielectric diminution of the interaction forces due to the part of the surface complex lying between the ions and the metal. Phenomenologically, it is possible simply to add to the interaction Hamiltonian (71) the effect of the dielectric effect of the intervening medium: the solvent sheath. It is evident that the transition probability would be simply

$$w'(k,\omega) = -(8\pi/\varepsilon'\hbar)\left|\mu_b'(k)\right|^2 \operatorname{Im} 1/\varepsilon(k,\omega), \quad (76)$$

where here the additional dielectric constant ε' is a strong function of the geometry of the interfacial surface complex system.

Consider now the evaluation of the matrix elements $(\rho_k)_{nc}$. (The evaluation to be given is based on the treatment of Pines--reference 77.) Both intra- and interband transitions are important contributors to $(\rho_k)_{nc}$,

but the most interest is directed to the interband transitions as they alone possess energy sufficient to excite surface complex transitions. The evaluation of $(\rho_k)_{no}$ is related to the determination of the sum rules satisfied by $1/\mathcal{E}(k,\omega)$. The sum rule satisfied by $(\rho_k)_{no}$ is

$$\sum_n (2m/\hbar k^2)\,\omega_{no}\,\left|(\rho_k)_{no}\right|^2 = N \qquad (77)$$

which is established through calculation of the expectation value

$$\left\langle 0 \left| \left[[\rho_k, H], \rho_k^{+} \right] \right| 0 \right\rangle . \qquad (78)$$

The evaluation of $[\rho_k, H]$ is

$$[\rho_k, H] = i\hbar\,\dot{\rho}_k = -\hbar \sum_i (\underline{k}\cdot\underline{p}_i/m + \hbar k^2/2m) \times e^{-i\underline{k}\cdot\underline{r}_i}, \qquad (79)$$

which is the equation of motion for ρ_k in the Heisenberg representation. The value of $[\rho_k, H]_{no}$ is given by

$$[\rho_k, H]_{no} = -\hbar\omega_{no}(\rho_k)_{no}. \qquad (80)$$

The expansion of (78) is

$$\sum_n \left\langle 0 \left| [\rho_k, H] \right| n \right\rangle \left\langle n \left| \rho_k^{+} \right| 0 \right\rangle - \left\langle 0 \left| \rho_k^{+} \right| n \right\rangle \left\langle n \left| [\rho_k, H] \right| 0 \right\rangle . \qquad (81)$$

The value of the commutator in (78) is $N\hbar^2k^2/m$, thus with (80) and (81)

$$\sum_n \left| \omega_{no} (\rho_k^+)_{no} (\rho_k)_{no} + \omega_{no} (\rho_k)_{no} (\rho_k^+)_{no} \right|$$

$$= \hbar N k^2/m. \qquad (82)$$

For systems invariant with respect to time reflection, (82) reduces to (77), and hence the sum rule is established. The invariance with respect to time reflection is, for these transitions, a statement of the principle of detailed balancing.

Expression (80) is used now in the evaluation of the interband transition matrix element. From (79) and (80) that matrix element is

$$\omega_{no} (\rho_k)_{no} = \left[\sum_i (\underline{k}.\underline{p}_i/m + \hbar k^2/2m)\, e^{-i\underline{k}.\underline{r}_i} \right]_{no} . \qquad (83)$$

In the limit, $k \longrightarrow 0$ for a transition from a state pv in one band to a state pℓ in another band, where

$$\hbar \omega_{\ell v}(p) = \epsilon_{\ell p} - \epsilon_{vp}, \qquad (84)$$

the matrix element becomes

$$\lim_{k \to 0} (\rho_k)_{no} = (\underline{k}.\underline{p})_{\ell v} / \omega_{\ell v}(p) m . \qquad (85)$$

From (77) it is seen that the longitudinal version of the Thomas-Reich-Kuhn sum rule is

$$\sum_n f_{no} = N, \qquad (86)$$

where

$$f_{no} = (2m/\hbar k^2)\omega_{no}\left|(\rho_k)_{no}\right|^2. \qquad (87)$$

The oscillator strength (87) evaluated by the use of (85) and averaged over all directions of k is

$$f_{no}(p) = \left\langle \frac{2m}{\hbar k^2}\frac{(\underline{k}.\underline{p})^2_v}{\omega^2_{\ell v} m^2}\omega_{\ell v}\right\rangle$$

$$= (2/m)\left|(p)_{\ell v}\right|^2/\hbar\omega_{\ell v}(p). \qquad (88)$$

Making use of the oscillator strength (87), it is possible to rewrite the expression (74) for the transition probability in terms of f_{no}

$$w(\underline{k},\omega) = (\pi/\hbar m\omega_{no})(4\pi e)^2\left|\mu_b(k)\right|^2 f_{no}$$

$$\times\ \delta(\omega + \omega_{no}). \qquad (89)$$

The appearance of transition probabilities of the form (74) bespeaks the close inter-relationship between current developments in solid state physics and electron transfer processes at electrode systems. The developments of this work indicate that in many instances the electrode system is indeed a part of a solid state system. To this point, an interesting observation as to the self-consistency of the two systems interacting upon each other can be made. If an electron transfer system at an electrode can be found in which chemical effects are minimized, or at least

well classified, it becomes clear that the fact that knowledge of the electronic transitions within the surface complex leads to knowledge of the dielectric response of the system. Likewise, knowledge of the dielectric response of the system leads to knowledge of the transition moments within the surface complex. It appears that on the basis of this observation new areas of investigation are possible. It appears possible that electrode systems may become new and powerful tools to add to the knowledge of solid state physics.

Having considered the transfer of energy from the metallic system to the surface complex, it is now necessary to consider the alternate possibility of the transfer of energy from the solution side of the interface. There are two prominent mechanisms to accomplish this. The first makes use of the transfer of energy of excitation from an excited species in solution to the surface complex. The second makes use of the inelastic collision of a molecule in the solution with the interface. The inelastic collision results in the conversion of kinetic translational energy to excitation energy. Consider now the first possibility.

The transition probability (45) given by Robinson and Frosch[73] is the starting point. The perturbation element can be formed by taking relevant terms of a multipole expansion of the 1/r interaction. As Robinson and Frosch[73] point out, however, this has limited applicability, especially with respect to the dipole-dipole term. Thus, we mention

the multipole expansion here only as an example. The reader is referred to the paper by Robinson and Frosch[73] for a more complete discussion, with additional references, of the problem.

The interaction term of the Hamiltonian is built from all the Coulomb interactions of the outer electrons of the centers A and B with the cores and with each other. The interaction leads to the van der Waal's forces, and is[61]

$$H' = (e^2/R^3)\left[\underline{r}_a\cdot\underline{r}_b - 3(\underline{r}_a\cdot\underline{R})/R^2\right] + (3e^2/2R^4)\left(\sum_{i=1}^{3}(R_i/R)r_{ai}^2 r_{bi}^2(-3 + 5R_i^2/R)\right) + \ldots . \quad (90)$$

Retaining only the first term in the expansion leads to the dipole-dipole approximation[61]

$$H' = (e^2/R^3)(x_a x_b + y_a y_b - 2z_a z_b). \quad (91)$$

From the expression (91) one finds the usual inverse sixth power law.

The transition probabilities dependent upon the energy transfer from the solution side of the interface then depend upon the matrix elements of (91). The matrix element of the interaction (91) averaged over all possible orientations gives[80]

$$\langle I|H'|F\rangle^2 = (e^2/R^3)^2(2/3)\left|\mu_a\right|^2\left|\mu_b\right|^2 . \quad (92)$$

In (92) μ_a is taken as the transition dipole moment of the transition in the surface complex, and μ_b, the transition dipole moment of the energy donating specie in the solution system. Where the dipole approximation breaks down for reasons of forbiddenness of transitions either in the energy donating or energy accepting system, higher terms of the interaction H', (90) must be used.[73,81] Such higher order interactions are of the dipole-quadrupole, and quadrupole-quadrupole, etc., type. In addition, where spin forbidden transitions are involved, it is necessary to make use of the spin Hamiltonian to describe the interaction. Discussions of the resulting matrix elements have been given by Dexter.[80]

The second possibility, that of energy exchange through collisions, is discussed now. There is clearly a close analogy here to the pressure exerted by a gas against the wall of its container. The number of molecules colliding with the interface having sufficient energy to excite the surface complex is Maxwellian. Let N be that number. Then there will be a number Z of molecules per unit time making collisions with the interface. Since the collisions are inelastic, there is a transfer of internal energy besides translational energy.

To get away from the idea of rough hard sphere collisions--which have been used as a model for inelastic collisions[82]--one need only realize that not every collision results in energy transfer. This is so because of the weak

interaction between colliding particles. Thus, the collision number, Z, is multiplied by some other number which gives the probability that a single collision results in energy transfer. The probability number can be given by expression (17), where it is assumed that there is an energy gap, i.e., a non-resonant process.[1] (The Landau-Zener coefficients, properly applied, could also be used.) In (17) there are two unknowns, H'_{12}, and t, which can be determined for the collision as follows. Let t for the collision be given by the lifetime of the collision complex; it will be of the order of 10^{-11} to about 10^{-14} seconds. As the colliding particles have mobile charges on them, the interaction can be described as one involving the Coulombic interaction of charged particles. The treatment to be given is admittedly qualitative, and is given only as an example. Let the free species, the molecules in solution, be described by plane-wave functions. If u represents the wavefunction of the surface complex, then the initial and final state wavefunctions are written

$$A\, e^{i\underline{k}_o \cdot \underline{r}_a}\, u_o(r_b)$$
$$A\, e^{i\underline{k} \cdot \underline{r}_a}\, u_1(r_b), \qquad (93)$$

where A is some normalizing factor which is convenient to set equal to unity, k_o is the wave vector of the incident particle having energy $E_o = \hbar^2 k_o^2/2m$, r_a and r_b are the electronic position coordinates of the particles a and b. Let the interaction be given by [69,83]

$$H' = - e^2 \sum_{j=1}^{n} \left| 1/r_{aj} - 1/r_a \right|. \qquad (94)$$

The matrix element H'_{12} is given by

$$H'_{12} = e^2 \iint d\tau_a d\tau_b \exp(i\underline{K}.\underline{r}_a) \left| 1/r_a - \sum_j 1/r_{aj} \right|$$

$$X \; u_o(r_b) u_1(r_b), \qquad (95)$$

where $K = k_o - k_1$. The integral, (95) can be evaluated making use of the fact that [83]

$$\exp(i\underline{K}.\underline{r}) = 1/K^2 \nabla^2 \exp(i\underline{K}.\underline{r}). \qquad (96)$$

Substituting expression (96) in equation (95) and making use of a double partial integration gives

$$H'_{12} = - (1/K^2) \iint d\tau_a d\tau_b \exp(i\underline{K}.\underline{r}) \left| \nabla^2(1/r_a) - \sum_j \nabla^2(1/r_{aj}) \right| u_o(r_b) u_1(r_b)$$

$$= 4/K^2 \iint d\tau_a d\tau_b \; u_o(r_b) u_1(r_b) \left| \delta(r_a) - \sum_j \delta(r_{aj}) \right| e^{i\underline{K}.\underline{r}_a}$$

$$= 4/K^2 \iint d\tau_a d\tau_b \; u_o(r_b) u_1(r_b) \left| 1 - \sum_j^b \exp(i\underline{K}.\underline{r}_j) \right|. \qquad (97)$$

For inelastic collisions, the first integral of the last expression in (97) is zero due to the orthogonality of u_o and u_1. The second term is expanded for $Ka \ll 1$--where a is the radius of the Bohr orbit--to give

$$H'_{o1} = (4\pi i/K^2) \int d\tau_b \, u_o(r_b) \sum_j^b r_j \, u_1(r_b), \qquad (98)$$

where the integral is the dipole moment for the transition o to 1. For the case Ka = 1, transitions to any state m are possible, including transitions other than dipole transitions.[83]

It is seen from equation (98) that the collisional exchange of energy between the surface complex and a fast species in solution is governed by the transition dipole moment of the transition in the surface complex. The first nonvanishing term of the expansion of (17) is

$$w(t) = 8H'^2_{12} t^2/\hbar^2. \qquad (99)$$

Replacing t by the lifetime τ of the order of 10^{-13} sec. it is seen that $H'_{12} < 0.5$ kcal/mole.[68] In order, then, for the electronic transition to be rate determining, the transition dipole moment must be fairly small.

The discussion in this chapter has been concerned with the evaluation of the proposed mechanisms of energy transfer between the system and the surface complex. It is clearly a difficult problem to determine which possible mode of energy transfer is dominant. The answer can only

be resolved by the careful choice of some experimental technique which focuses upon, and clearly reveals, one particular mechanism. However, in spite of the lack of a concrete choice of mechanism, one is heartened by the fact that no matter which mechanism is chosen, ultimately the rate constant can be shown to depend in part on the transition moment of the rate-determining transition in the surface complex. This certainly is some accomplishment. It is fortunate also that the rate constant, depending as it does on the total matrix element, contains all perturbations. The total perturbation appears as a sum of individual perturbations. Since the transition moment of the surface complex appears in each perturbation, it is possible to factor it out leaving an average effect of the surroundings coupling with the surface.

CHAPTER V

DIRECT CHARGE TRANSFER, ELECTRODEPOSITION, AND ELECTRODISSOLUTION

In the preceeding three chapters attention has been focused on the consequences for charge transfer when two assumptions concerning the mechanism are made: one, the assumption of an ordered interfacial system, and two, the assumption that there are solvate molecules responsible to a large part for the charge transfer.

Consideration of charge transfer to species associated with the electrode surface, but not through a solvent sheath, must bring into the picture other kinetic factors. There seems to be evidence that certain electrode processes take place at the electrode directly without benefit of an intervening solvent layer. (Discussions on the adsorption of ions and neutral species on electrode surfaces and their effect on the kinetics of charge transfer can be found in papers by Frumkin,[84] Grahame, Higinbotham, and Deane,[85] Llopis, Fernandez-Biarge, and Perez-Fernandez,[86] and Delahay.[87] See also the book by Delahay--reference 88--and articles by Bockris and Swinkels.[89,90]) This is apparently so for anions and for neutral organic species such as aromatics. It appears that for most of these substances the solvation energies are so miniscule and the adsorption energies are so much larger that adsorption is a much better competitor for the reactive species.[91]

Consequently, the reaction takes place directly on the surface. For the theory of charge transfer previously given to be general, it must be shown that it can accomodate these special reactions.

One can, if one wishes, retain the ideas concerning the ordered interfacial structure developed in the previous chapters. However, for direct charge transfer from the electrode surface to the adsorbed species this has little meaning or use, as the adsorbate will conform to the electrode surface structure anyway. Without reference to any detailed description of the associations or bonding which may take place between the metal surface and the reactant, it is possible to derive the current expressions and the equilibrium condition--the Nernst equation--by considering the following picture of the interfacial system.

First, consider the charge transfer state to be an excited state of the system of metal and reactant while the reactant and product are still associated with the metal surface. No more need be said about this excited state for the present other than the fact that when the product leaves the surface the electron must remain with the product. This assumes, of course, that this is the direction of the reaction. (Obviously, if the reaction is an oxidation, the electron must remain with the electrode; it was originally excited from the adsorbate.) Consider second, two limits which lead to two forms of the current. The limits are: one, rate, and hence current, governed by

the charge transitions in the transfer steps, and two, rate governed by the vibrational factors involved in the removal of the product from the surface. In other words, vibrational factors lead to chemical and not electronic rates.

In terms of the radiation analogy (Chapter II) the current expressions can be expressed through use of the Einstein transition coefficients. Considering the first limit given above, the current expressions take on the following form. Consider, for example, that the current direction leading to the formation of a reduced species of an originally neutral species (e.g., to a radical anion) requires energy. Denote the energy of the transition by E_{12}, where E_1 is less then E_2, which are the initial and final states respectively. The forward current can be written very simply as a function of the induced absorption coefficient:

$$i_f = A\mathfrak{F}CB_{12}\rho(\omega_{12}). \qquad (1)$$

In the low temperature limit the radiation density is given by II(13). The principle of detailed balancing leads to the final form of the forward current

$$i_f = A\mathfrak{F}CA_{21}\exp(-E_{12}/kT). \qquad (2)$$

The lifetime of the excited state is given by $\tau = 1/A_{21}$, which allows (2) to be written as

$$i_f = (A\mathfrak{F}C/\tau)\exp(-E_{12}/kT). \quad (3)$$

The reverse current is given by

$$i_r = -A\mathfrak{F}C^-(B_{21}\rho(\omega_{12}) + A_{21}). \quad (4)$$

In the low temperature limit equation (4) becomes

$$i_r = -(A\mathfrak{F}C^-/\tau). \quad (5)$$

Expression (5) simply states that the induced emission factor is negligible.

The total current is given by

$$I = i_f + i_r = A\mathfrak{F}/\tau(C\exp(-E_{12}/kT) - C^-), \quad (6)$$

and at equilibrium I = 0. From that condition one finds the form of the Nernst equation to be the following:

$$C^-/C = \exp(-E_{12}/kT). \quad (7)$$

Making the identification $NE_{12} = -n\mathfrak{F}\mathcal{E}$ in (7) given the form

$$\mathcal{E} = (RT/n\mathfrak{F})\ln(C/C^-), \quad (8)$$

where in the identification of the energy above, N is the conversion factor taking electron volts to kcal/mole.

In the second limit, the electronic transitions are much faster than the chemical rates, and the electronic transitions create a steady state population of some intermediate. The current is assumed not to be realized

until a chemical step has taken place. It is readily seen that equation (7) is the equilibrium concentration of C^- at the electrode. In terms of a general chemical rate constant,

$$k_{chem} = k^{\circ}_{chem} \exp(-E_a/kT), \tag{9}$$

where E_a is the activation energy for the chemical step, the forward current becomes

$$i_f = A\mathfrak{F}Ck^{\circ}_{chem} \exp[-(E_{12} + E_a)/kT . \tag{10}$$

The reverse current remains that given by expression (5). In terms of the equilibrium condition, I = 0, the Nernst equation becomes

$$\mathcal{E} = (RT/n\mathfrak{F}) \ln (1/k^{\circ}_{chem}\tau) + (RT/n\mathfrak{F}) \ln (C^-/C), \tag{11}$$

and $\mathcal{E} = \mathfrak{F}N(E_{12} + E_a)$. The expression for the total current is

$$I = A\mathfrak{F}\left[(C/k^{\circ}_{chem}) \exp[-(E_{12} + E_a)/kT + C^-/\tau\right]. \tag{12}$$

When an external potential is applied to the electrode system, however, the situation is altered. From the previous discussion of the effect of an external polarization (Chapter II), the current expression is expected to have the form

$$I = A\mathfrak{F}\left[(C/k^{\circ}_{chem})\ \exp-(E_{12} \pm \underline{m}_{12}\cdot\underline{E} + E_a)/kT + C^{-}/\tau\right], \qquad (13)$$

where $\underline{E}$ is the polarization field applied to the system, and $\underline{m}_{12}$ is the transition moment of the 1 to 2 transition. The external potential alters only the equilibrium concentration ratio of C/C^{-}. (When an external potential is applied to the electrode system.) It has been stated that then the system makes an attempt to adjust the concentration ratios of electroactive species to come to a new equilibrium situation. In the interim, while making the transition to the new equilibrium state, the system is dynamically controlled. It is for this reason that one expects the chemical rate factors to play the most important role.

With the above points in mind further generalizations are made concerning direct electron transfer at electrodes. Consider the sequence of steps

$$\begin{aligned} A + el &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A\text{-}el \\ A\text{-}el &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^{-}\text{-}el \\ A^{-}\text{-}el &\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A^{-} + el, \end{aligned} \qquad (14)$$

where A is a neutral reactant, and el represents the electrode.

A-el and A^--el represent the two forms of the surface complex. Assuming the steady state concentrations of surface complex forms, the form of the Nernst equation, (8), can be re-expressed as

$$\mathcal{E} = (RT/n\mathcal{F}) \ln (k_{-1}k_{-3}/k_1k_3) + (RT/n\mathcal{F}) \ln (C^-_o/C_o), \qquad (15)$$

where the C_o are the bulk solution concentrations. Equation (15) adds nothing essentially new. It merely expresses the concentration of the surface complex in terms of the bulk concentration. The expression (15) becomes, for specific evaluation, merely the potential dependent on diffusion and other chemical factors. At an equilibrium situation it is expected that the first term on the right is zero as the ratio of the rate constants is approximately unity.

From the sequence (14), however, it is possible to revise the current expression under the influence of an external polarization depending on the direction of the polarization. Suppose that the direction of polarization is such as to lower the potential with respect to the original equilibrium potential. Thus, in equation (13) the $-\underline{m}_{12}\cdot\underline{E}$ will be effective, and the expression will remain as it is. The chemical rate constant, k^c_{chem}, is identified with k^o_3, which is the rate of break-up of the surface complex in its reduced form. If the polarization

is such, however, that the potential is raised with respect to electronic transitions from the electrode, then the reverse charge transfer will be favored, and the current assumes the form

$$I = A\mathcal{F}\left[(C/\tau)\exp(E_{12} + \underline{m}_{12}\cdot\underline{E})/kT + k^{\circ}_{-3}C^{-}\exp(-E_{-3}/kT)\right]. \qquad (16)$$

The interpretation of (16) is simply that the rate of reverse electronic transition is so fast that the current becomes governed by the rate of incorporation of the anionic species or organic species into the interfacial system. Thus, one concludes that under conditions of nonequilibrium, the current, which reflects directly the rate of reaction, is determined predominately by chemical factors. At the equilibrium situation where the chemical factors, on the average, cancel one another, the potential and the exchange currents reflect the direct electron exchange process, and not the chemical effects.

Consideration of the direct reaction of anionic species at an electrode poses no new problems as far as the general model presented is concerned. The current expressions presented in the first part of this chapter can be taken over here with the provision that the electron coming from the anion will generally be of lower energy with respect to the metal Fermi level. The energy consuming step is thus the transition from the ion to the electrode.

For organic and anionic species reacting at the usual electrode materials, e.g., mercury, platinum, etc., there is considerable evidence from both electrochemical and adsorption studies that the associations are not strong in most cases.[89-91,92,93] This seems to be especially true for neutral organic reactants. These relatively weak associations between the metal and the neutral organic substrate have been treated with comparative success using charge transfer concepts. A charge transfer association will also be assumed to be operative between the metal and the anionic substrate.

The details of the formation of the charge transfer bond can be elucidated in terms of Flurry's MO treatment.[94] Take ϕ_m to be the highest filled surface state wavefunction without assuming any interaction specifically due to the reactive species. The wavefunction ϕ_s is the lowest unfilled MO of the reactive species without being altered by the presence of the metal surface. These free species' wavefunctions become changed through mutual interaction. The Hamiltonian for the reactant species perturbed by the presence of the surface is

$$H_r = H_r^o + V_m . \qquad (17)$$

Likewise, the Hamiltonian for the perturbation on the metal surface caused by the presence of the reactant is

$$H_m = H_m^o + V_{eff}, \qquad (18)$$

where V_{eff} is the effective perturbation potential seen by the metal due to the reactant.

In Flurry's method,[99] the ground state wavefunction for the surface complex is written

$$\phi_N = a\phi_m + b\phi_s. \tag{19}$$

The electronic ground state energy is given by

$$W_N = a^2\langle m|H_{op}|m\rangle + b^2\langle s|H_{op}|s\rangle + 2ab\langle m|H_{op}|s\rangle. \tag{20}$$

The Hamiltonian, H_{op}, is given by

$$H_{op} = H^{\circ}_m + H^{\circ}_s + H'_m + H'_s, \tag{21}$$

where H°_m and H°_s are the free species Hamiltonians given by (17) and (18). The terms H'_m and H'_s are the combined perturbation effects of (17) and (18) plus any additional perturbations arising when the two subsystems are brought together. When the two systems are brought together to form a complex, it is necessary to add a term V_{es} which results if a complete charge transfer takes place between donor and acceptor. The ground state energy now becomes

$$E_N = a^2\langle m|H_{op}|m\rangle + b^2\langle s|H_{op}|s\rangle + 2ab\langle m|H_{op}|s\rangle - b^2V_{es}. \tag{22}$$

Let

$$M = \langle m|H_{op}|m\rangle$$

$$S = \langle s|H_{op}|s\rangle$$
$$\beta_{ms} = \langle m|H_{op}|s\rangle , \qquad (23)$$

then equation (22) becomes

$$E_N = a^2M + b^2S + 2ab\beta_{ms} - b^2V_{es}. \qquad (24)$$

The excited state wavefunction is given by the expression

$$\phi_E = b\phi_m - a\phi_s. \qquad (25)$$

Where a and b have the same values as in (19)--approximative--the energy of the excited state is written immediately

$$E_E = b^2M + a^2S - 2ab\beta_{ms} - a^2V_{es}. \qquad (26)$$

The energy of the charge transfer transition is $E_E - E_N$, and is given by

$$E_{ct} = (b^2 - a^2)(M - S + V_{es}) - 4ab\beta_{ms}. \qquad (27)$$

For small β_{ms}, and for a small amount of charge transfer in the ground state, the usual Murrell expression for the charge transfer can be used:[64,99]

$$E_{ct} = \phi - EA + C, \qquad (28)$$

where in (28) ϕ is the work function of the metal, and EA the electron affinity of the substrate on the surface. (For oxidative reactions the expression (28) assumes the form $I - \phi + C$, where I is the ionization potential of the substrate on the surface.)

Flurry, in a subsequent paper,[95] has presented an evaluation of the V_{es} term. V_{es} is dependent on the nature of the components making up the charge transfer complex, and thus is dependent on the charges on the two. From Flurry's paper[95] it is found that for both components neutral, the charge transfer transition energy is approximated by

$$E_{ct} = (b^2 - a^2)(M - S + Z_m^{eff}\langle s|1/r_m|s\rangle) - 4ab\,\beta_{ms}, \qquad (30)$$

where Z_m^{eff} is the effective nuclear charge on the metal, assumed to be the donor. (If the metal is the acceptor, then the terms are reversed and $S - M + Z_s^{eff}\langle m|1/r|m\rangle$ replaces the value in the parentheses above.) The distance of the donor electron from the donor nucleus is r_m.

For an anionic donor species, the charge transfer energy is

$$E_{ct} = (b^2 - a^2)(M - S) - 4ab\,\beta_{ms}. \qquad (31)$$

The values of M and S for expression (31) cannot be taken directly from the tables of the ionization potentials, the electron affinities, and the work function. The quantities M and S contain factors accounting for the effect of solvation. However, if the resonance integral is small, in the expression (29) the factor C should be predominately the energy of solvation.

As a conclusion to this chapter electrodeposition and electrodissolution are discussed. These two processes are closely related to the chemically controlled direct reactions discussed earlier in this chapter.

Assume a monovalent ion of the type where a one electron transition is needed to produce the metal atom. The mechanism of electrodeposition will then be such that the ion will first be reduced to the solvated metal atom which subsequently will become a part of the electrode surface through a free radical-like collision reaction. The new species, in the case of electrodeposition, will be the new surface formed and covered by adsorbed solvent molecules.

In the derivation of the current expression for the electrodeposition, it is assumed that the rate-determining step is the free radical-like encounter reaction. In other words, it is assumed that the production of solvated, unencountered metal atoms is steady state. This means that the number of reduced, solvated metal atoms is given by

$$C^{\circ} = C^{+}(A_{io}/A_{ir}) \exp-(E_{oi} - E_{ri})/kT, \qquad (33)$$

where C° is the concentration of reduced solvated metal atoms, C^{+} the concentration of unreacted ions in the interface, and the A_{io} and A_{ir} have the same meaning as in Chapter II. The forward current is given by

$$i_f = A\mathfrak{F}C^{\circ}k_{en} = A\mathfrak{F}C^{+}k^{\circ}_{en}(A_{io}/A_{ir}) \exp-(E_{oi} - E_{ri} + E_{en})/kT, \qquad (34)$$

where k°_{en} is the rate of encounter of the solvated atom with the surface of the electrode. The reverse current is given by (with $A_{io} = 1/\tau$)

$$i_r = - A\mathfrak{F}c^{\circ}/\tau = - A\mathfrak{F}c^{+}(1/\tau)(A_{io}/A_{ir}) \exp-(E_{oi} - E_{ri})/kT. \quad (35)$$

Thus, the total current is

$$I = A\mathfrak{F}c^{+}(A_{io}/A_{ir}) \exp-(E_{oi} - E_{ir})/kT \left[k^{\circ}_{en} \exp(-E_{en}/kT) - 1/\tau\right], \quad (36)$$

which can be written as

$$I = A\mathfrak{F}c^{+}(1/\tau)(A_{io}/A_{ir}) \exp-(E_{oi} - E_{ri})/kT \left[\tau k^{\circ}_{en} \exp(-E_{en}/kT) - 1\right]. \quad (37)$$

The reverse process of electrodissolution is treated analogously. Assume that on the surface of the metal there are a number of partially solvated metal atoms. Assume further that there is an electronic excited state of this system in which the electron is essentially removed from it. If there is a vibrational mode of this system which leads to the breaking off of the partially solvated, partially positive atom, then it is presumed that once free from the surface the ion picks up the remainder of its solvation sphere and is fully charged. Denote the number of partially solvated surface atoms by S. Further, the number of these

in the excited state are given, in the low temperature approximation, by a Boltzmann population:

$$S^* = S \exp(-E_s/kT). \tag{38}$$

The current is assumed to be dependent on the rate of removal of the partially solvated, partially positive atom, and is given by

$$i_s = - A\mathfrak{F}S\, k^{\circ}_s \exp-(E_s + E_a)/kT, \tag{39}$$

where E_a is the activation energy of the dissolution step. The reverse current is given simply by

$$i_r = A\mathfrak{F}S^*/\tau = (A\mathfrak{F}S/\tau) \exp(-E_s/kT). \tag{40}$$

The total current is

$$I = - (A\mathfrak{F}S/\tau) \exp(-E_s/kT) \left[\tau k^{\circ}_s \exp(-E_a/kT) - 1\right], \tag{41}$$

which is essentially the same form as (37).

CHAPTER VI

PHOTOEFFECT AND INTERFACIAL SPECTROSCOPY

Except for a consideration of the application of an external polarization potential, the discussion has been restricted only to energy transfer to the interfacial system from the surroundings, i.e., the metal and the solution. There is the possibility of introducing energy into the system from the outside through an external light source. If the transitions involved in the transfer of charge from the electrode to the ion are real, then one expects that an external light source would be able to excite transitions preferentially with light of a wavelentgh corresponding to the transition. Considering that the transitions exist, an equilibrium electrode system under the influence of an external light source might exhibit the behavior depicted in Figure 8. That more than one peak might be observed is a consequence of the fact that there is the possibility of more than one transition, which, under the influence of the external excitation, may be rate-determining. Thus, one expects that a spectrum of the interfacial state would be obtained from a plot of the current versus wavelength of exciting light. The current in this case is a direct representation of the intensity of the absorption of the charge transfer transition.

The photoeffect expected for an electrode system is not the usual photoeffect observed at a bare metal surface.

Figure 8

A plot of the current versus wavelength dependence expected for the electrode photoeffect. Such a dependence presumes the existence of real transitions leading to the currents. (The solid line represents the current, and the dashed line represents the reciprocal photoelectric absorbancy.)

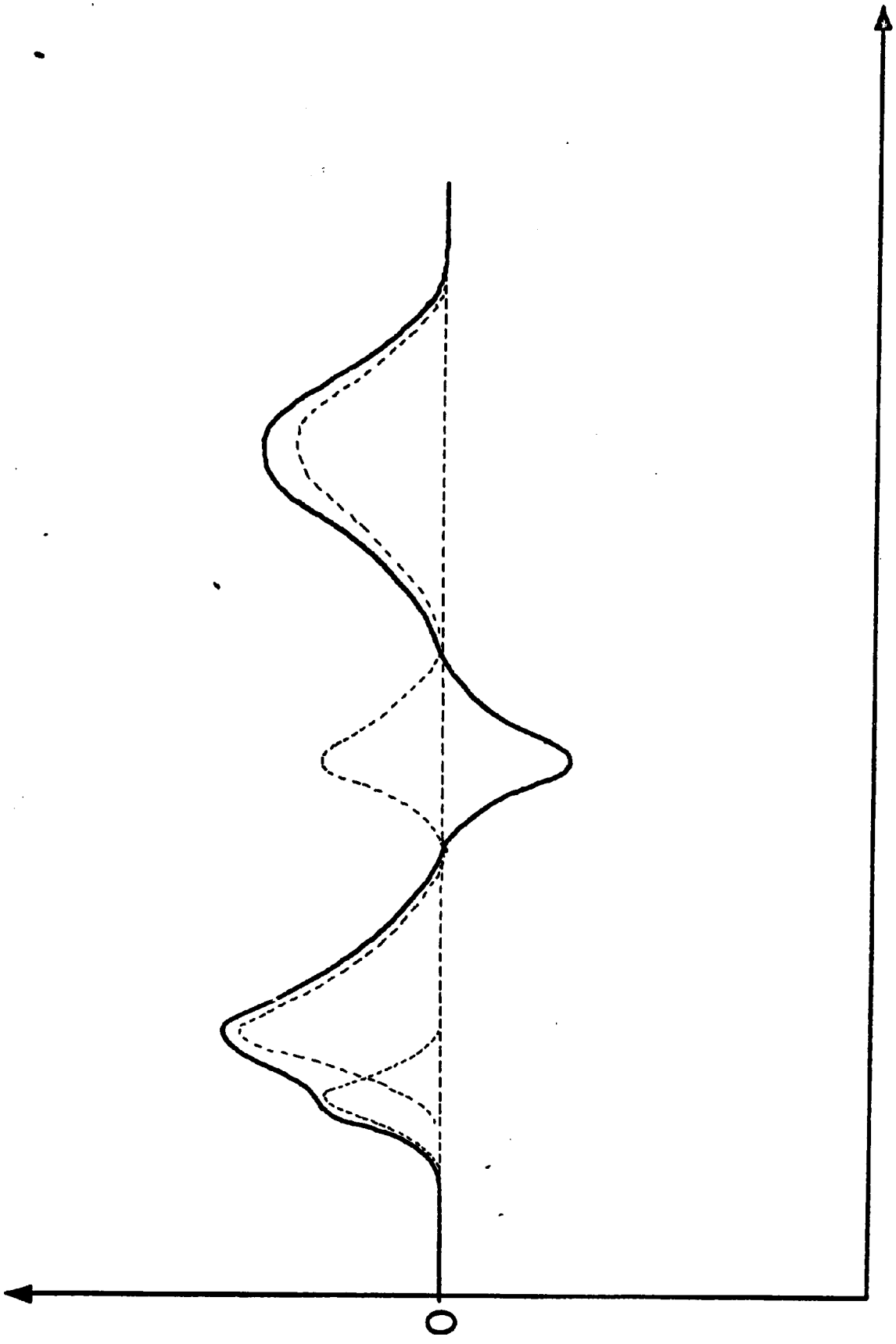


Figure 8

This is, of course, due to the assumption that there is a molecular structure in the interfacial system.

With the assumption that the photoeffect at an electrode leads to a "spectrum", which, for all considerations, is a real spectrum of the charge transfer transitions, one can define for these transitions an oscillator strength. The oscillator strength can serve in the classification of an electrode reaction. Thus, not only will one be able to obtain the energies of the respective transitions, but also the intensities.

The analysis runs as follows. Formally, there is a close relation between the photocurrent observed (expected, of course) and the diminution of intensity of radiation passing through an absorbing body. The diminution in intensity normally observed for light passing through a sample is given by the Lambert-Beer law. Assuming that the electrode system is in a state of equilibrium, then the application of an external light source is expected to cause a current flow different from the equilibrium exchange current. Depending upon which transition is excited, the current will correspond presumably to only one excitation. For every electron contributing to the current one can assume that one photon has caused an excitation. The analysis of the photoeffect is made by employing the Lambert-Beer law modified in such a manner that the current accounts for the absorbed radiation. (The discussion which

follows relies fairly heavily upon the unpublished lecture notes of S. M. Blinder--reference 96.) The Lambert-Beer law in its integrated form is

$$\ln(I/I_o) = -\alpha(c)\ell, \qquad (1)$$

where α is the molar extinction coefficient, (c) the concentration of absorbing species, and ℓ the path length of the "cell"--here the cell would correspond to the distance to the first Helmholtz plane. The incident intensity is I_o and the intensity of light reflected from the electrode surface is I. The intensities are balanced by writing

$$I_o = I + CJ, \qquad (2)$$

where J is the current observed, and C is a constant which converts units of current (amperes) to units of intensity. Measuring intensity as particles per unit area, it is easy to see that C should be approximately 6.25×10^{18} sec-photons. It is now possible to rewrite the Lambert-Beer law as

$$\ln((I_o - CJ)/I_o) = -\alpha(c)\ell = \frac{1}{\text{photoelectric absorbancy.}} \qquad (3)$$

In Figure 8 the representation of the expected behavior of (3) as a function of wavelength is given. The expression (3) can now be used to obtain the oscillator strengths of the charge transfer transitions. This is shown by reviewing the usual treatment.[96]

If, as usually occurs, there is a fairly broad band at a particular absorption, the Lambert-Beer law is expressed in terms of the integrated molar extinction coefficient $\alpha(\bar{\nu})$ over the width of the band. Thus,

$$\ln((I_o - CJ)/I_o) = -(c)\ell\int d\bar{\nu}\,\alpha(\bar{\nu}). \tag{4}$$

From the semiclassical treatment of radiation, using time-dependent perturbation theory, the transition probability per unit time is given by

$$w_{km} = (4\pi^2/3\hbar^2 c)\, I(\omega_{km})\left|\mu_{km}\right|^2, \tag{5}$$

which is easily transformed to cm^{-1}

$$w_{km} = (2\pi/3\hbar^2 c^2)\, I(\bar{\nu}_{km})\left|\mu_{km}\right|^2. \tag{6}$$

(In the above expressions (5) and (6) c is the speed of light.) The diminution of intensity of light passing through the interfaical system is

$$-dI = w_{km}\hbar\omega_{km}\, n\, dx, \tag{7}$$

where $n = N_o/1{,}000$. Thus,

$$-dI = (2\pi/3\hbar^2 c^2)\, I(\bar{\nu}_{km})\left|\mu_{km}\right|^2 2\pi\hbar c\bar{\nu}_{km}\, n\, dx, \tag{8}$$

and integration gives the Lambert-Beer law:

$$I = I_o \exp\left[-(4\pi^2/3\hbar c)\bar{\nu}_{km}\left|\mu_{km}\right|^2 n\ell\right], \tag{9}$$

where from (9) one finds,

$$\int d\bar{\nu}\, \alpha(\bar{\nu}) = (4\pi^2/3\hbar c) \left|\mu_{km}\right|^2 . \qquad (10)$$

From (10) one may obtain experimental values for the transition moments of the charge transfer transitions--providing, of course, that such a representation as has been assumed does exist. The Thomas-Reich-Kuhn sum rule is[83]

$$f_{km} = (2m/3\hbar)\omega_{km} \left|\underline{r}_{km}\right|^2 . \qquad (11)$$

Substitution of expression (11) into (10) and solving for f_{km} one finds

$$f_{km} = (1{,}000\ mc^2/\pi N_o e^2) \int d\bar{\nu}\, \alpha(\bar{\nu}_{km})$$

$$\cong 10^{-9} \int d\bar{\nu}\, \alpha(\bar{\nu}_{km}). \qquad (12)$$

It is hoped that if the photoeffect occurs as predicted it will be possible to characterize the electrode system with much greater accuracy than has previously been known.

The photoeffect discussed thus far has been assumed to be dependent on electronic transition energies within the surface complex. There is also the possibility that the photoeffect may be involved in the acceleration of chemical processes at the electrode, i.e., the vibrational factors connected with electronic transitions. This is expected to be a major factor in cases where the current can have an almost total dependence on a chemical rate step. As these chemical steps may involve the breakage of relatively strong associations between the electro-

active species and the electrode, the energies involved are most likely to be at least of the magnitude one usually observes for the electronic spectra. It may prove difficult to separate some of these effects from the purely electronic effects. One can only hope to expect that the vibrational factors in the interface, associated with the bonds between species, may be more susceptible to changes in environment than the electronic transitions. Changing the environment would then show which effects observed correspond to chemical factors.

With respect to the experimental observation of the photoeffect, it is important to note that the imposition of a light source is similar to the imposition of an external potential on the electrode. It is assumed that the electronic transitions are responsibie for the transfer of charge between species. The difference between reactant and product is one unit of charge. Thus, a photon absorbed by the surface complex system leading to a charge transfer has forced the interfacial system to a new Nernst condition. The bulk of the solution, however, is out of balance with the interface, and the driving force is the difference in chemical potential. As a result of the driving force, the system becomes diffusion controlled. Now, if the photoimpulse is of sufficient duration, the intensity relations given by (10) and (12) no longer hold for the original equilibrium distribution of reductant and oxidant. Thus, to obtain meaningful intensities for the electrode photo-

effect at an arbitrary equilibrium distribution of reactants, it is necessary that the photoimpulse be of duration shorter than the response of the system to diffusion controlling processes. It is possible that an analysis of these diffusion processes would lead to a means of subtracting their effect, thus leaving one with the true electronic response of the interfacial system. It seems more reasonable, however, to perform the experiment by a pulse technique, and to study the response of the system on the steep ascending slope (c.f. Figure 9). Adjusting the experiment to give unit intensity at each pulse and at each arbitrary wavelength along the scan would be expected to give the curve in Figure 8. Breaking off the current measurement at the cessation of the pulse would give the maximum intensity for that pulse as measured by the current. Experimentally, the break-off point for the measurement could be triggered electronically by taking the rate of change of the initial ascending slope. It is presumed that this would work since the initial electronic transition response to the photoimpulse is expected to be linear. Such a system would end the measurement at the onset of the diffusion controlled process.

In addition to the photoeffect there exists the possibility, and now a reality,[97] of using internal reflectance absorption spectroscopy to obtain the total spectrum of the electrode interfacial state. It is presumed that the photoeffect specifically characterizes the charge transfer

Figure 9

The current versus time response expected for an illuminated photoelectrode.

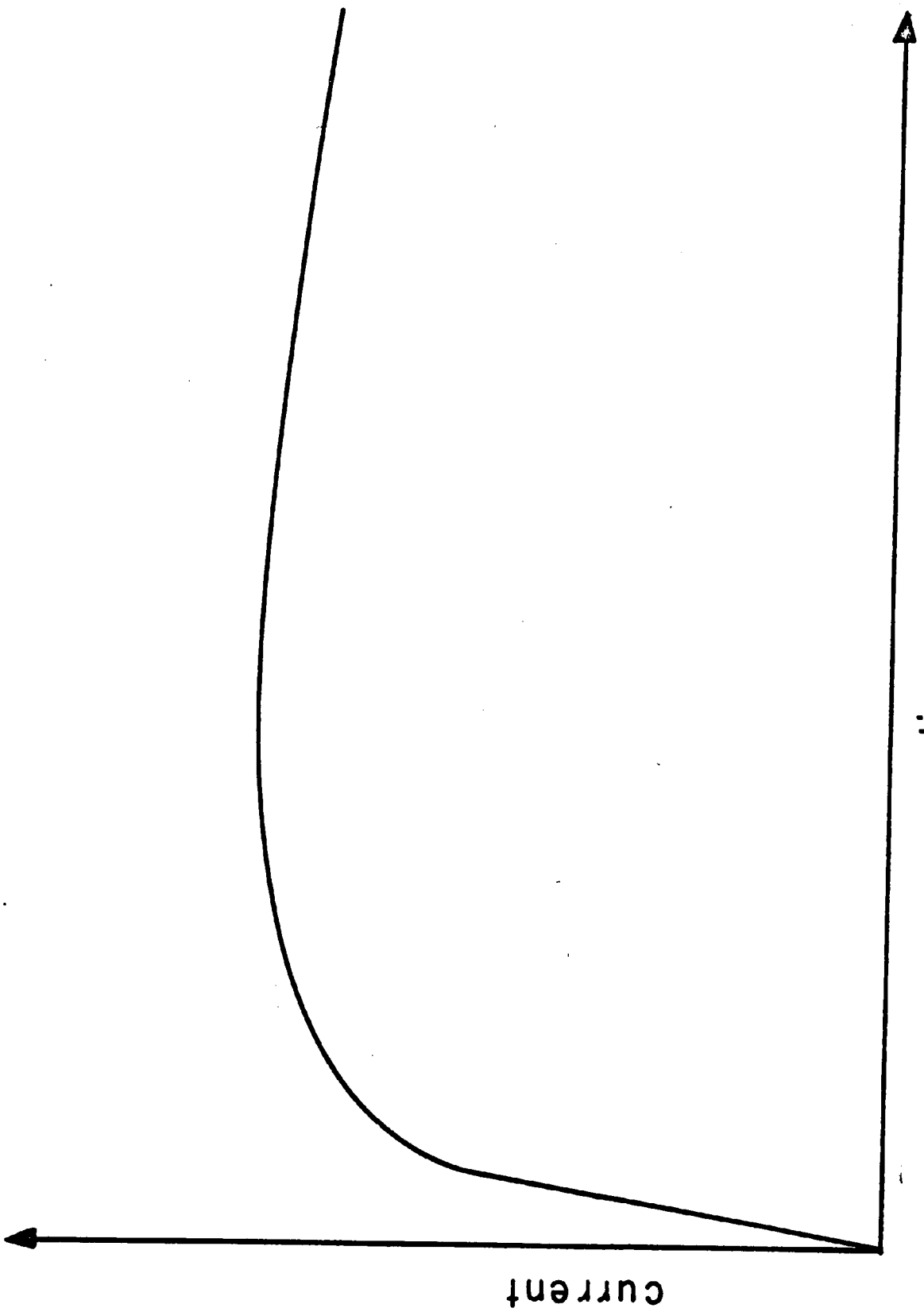


Figure 9

transitions. In the remaining paragraphs a list of predictions is given based on the model assumed. These predictions are precisely that which one would expect to find experimentally on performing a spectroscopic examination of the interface.

With reference to the systems discussed in Chapter III assume first the non-conjugated system. The use of internal reflectance spectroscopy can be expected to give in particular all transitions within the solvate-ion complex. Knowing this for one electrode, say a platinum electrode, it is of interest to examine the results expected on changing electrodes. (Of great interest in this area would be the investigation of electrode reactions on definite metal crystal faces. Work on the behavior of metallic single crystals has been given by Piontelli, Poli, and and Serravalle.[98]) On going from one electrode system to another, say in this case palladium, one reasonably expects that the new electrode represents a slightly different perturbation. If the new metal electrode has the same crystal face, and if one can presume that the same orbitals are used throughout, then one should be able to predict the change in the spectrum of the surface complex due to the slight alteration caused by changing electrodes. On an average over all space directions the change should show up for polycrystalline material also. The change is expected to show up most in the intensities, and not nearly so much in the position of the absorption maxima--

unless the work functions of the two different metals differ greatly. The change in intensity reflects directly the change in transition moment, and hence can be given by

$$\underline{M} = \sum_m \frac{H'_{mk} \underline{M}_{nm}}{E^o_k - E^o_m} + \sum_m \frac{H'_{mn} \underline{M}_{mk}}{E^o_n - E^o_m} , \qquad (13)$$

in which the $\underline{M}_{pq}$ are the transition moments on the original metal. The H'_{pr} are the perturbations found on changing metals.

Assuming still the same non-conjugated system, one expects dramatic differences if one takes the same ion-solvate system spectrum over electrodes in which the association between ion-solvate and metal is grossly different. These differences do indeed show in the rates of electrochemical reactions.[99] The differences in rates have been accounted for in a systematic manner recently by Gierst[99] making use of Gurney's[100] rule relating ion pair formation to ion size and effective ionic charge.

Assume now the latter case, that of allowing conjugation. One expects that the spectrum will show more specifically the charge transfer transitions. In addition, the effect of the charge transfer transitions will show up in the general spectrum of the surface complex. This follows directly from the model used, based on the Longuet-Higgins and Murrell[65] treatment. If it were possible to obtain the complete charge transfer spectrum from the photoeffect, then it would be possible to determine the percentage of

mixing of charge transfer transitions with other locally excited configurations.

It is an unfortuante limitation of the electrode system that the reactive species cannot be removed from the interface, preserving their geometry, and examined by the usual spectroscopic techniques. The only means, it appears, of making predictions about the structure of the complexes in the interface is to assume ligand geometries and perform the requisite calculations of the energy levels. Comparison between the calculated and observed transitions would give indirect evidence of the structure.

A possible further means of making some interpretation of the structure would come from the expected changes in structure in going from different equilibrium ratios of reactant to product ion. This, it will be recalled, leads, on assumption, to the expectation of different structures. Because of the continuous nature of the potential over the concentration range, however, it is expected that changes in structure will not be drastic--abrupt changes in structure would be expected to lead to abrupt changes in potential. The changes expected might be likened to the nature of the continuous change in going from a tetragonally distorted crystal field to a square planar one. This can be done in a continuous manner by slowly removing point charges on opposing vertices of the octagon. Thus, for an electrochemical system, the method of obtaining structural information would be to assume two or more possible configurations

for the solvate about the ions. Performing the calculations on these, one could then note the theoretically predicted change in configuration of solvate for a progressing change in potential. Comparing the theoretical predictions with experiment then would justify either the acceptance or rejection of the theoretically assumed structures.

Caution must be exercised in the assignment of geometries to the solvate structure in the interface for the following reason. It was seen in Chapter III that the effect of the electrode surface atoms acting on the solvated ions in the interface could be viewed as an additional point charge in a crystal field. Thus, in the example given there, a tetragonal field of solvate about the ion is distorted by the image charge on the electrode, and the splitting of the d levels in the ion itself resembled more that of a trigonal bipyramid, not that of the tetragonal field of the solvate molecules.

Situations of the type imagined for this example might be expected to be strongly dependent on the polarity and the magnitude of the potential on the electrode surface. Thus, if by some pulse technique it would be possible to change the potential on the electrode and examine the spectrum in the time less than it takes for the chemical effects to begin to alter the makeup of the interfacial state, it would be possible to make some definitive measurement leading to a statement of the real structure of the solvated ion in the interface. With sufficiently rapid

pulse techniques, and a sufficiently sensitive spectroscopic instrument it should be possible to force the complex to exhibit its true spectrum by placing a charge, for an instant, on the electrode which negates the image charge of the solvated ion.

There are cases, however, in which the spectrum taken of the solvated ion in the interface is expected to conform to the true structure of that ionic complex. Such a configuration of metal, solvate and ion is shown in Figure 6. Here each solvate molecule is associated almost entirely with an individual metal atom. The effect of each metal atom, in a classical electrostatic sense, in juxtaposition to the solvate molecule, is merely to alter the effective charge on that molecule. If the alteration is not too great, the spectrum is expected to be "true".

The two examples mentioned here serve to illustrate a very important point. That point is that in many instances the spectrum taken of the components of the interfacial state for one electrode potential cannot be relied upon to give meaningful information by itself. In order to obtain meaningful information about the electronic and geometric structure of the interfacial components it is mandatory that the effect of the potential be taken into account. Whereas in the free species complex ion the only important perturbation on the central ion is the molecular crystal or ligand field, in the interfacial state the perturbation on the surface and its polarizable charge are of equal

importance to that of the original crystal field.

As with the photoeffect, so it is with the spectroscopic measurement, i.e., the light entering the interfacial system has an effect similar to the imposition of an external potential. In the equilibrium system electronic factors are presumed rate-determining. If, however, an external potential is applied to the electrode while the spectroscopic measurement is being made, and if the effect of the applied potential is stronger than the intensity of light entering the interface, then the system will realize the Nernstian equilibrium condition dictated by the potential, and not by the light source. The perturbation of the light source is thus much weaker in its effect than the mass action dynamics and the applied potential which work to keep the local Nernstian condition in the interface. The spectrum taken of the interface under these conditions should not be bothered by the additional light source from the spectrometer.

A problem closely allied to the photoeffect and spectroscopy of the interface is that of electroluminescence. Recently, Marcus has discussed the possibility of electrode luminescence based on conclusions drawn from the application of his theory.[101] There are two possible routes an electrode system could take to luminesce. The first is the possibility of an optical photon produced by the relaxation from the excited intermediate configuration to the ground configuration of the reduced ion in the interface. Such a transi-

tion would proceed with a minimum of energy loss through conversion of electronic to vibrational energy--or so it is presumed. The second process is contained in the possibility that the reduction electron having been promoted from the metal to the excited intermediate configuration remains with the product species in an excited state after the species has been removed from the electrode surface. This presumes that the association between the product and the electrode is weak, and that the intermediate configuration relaxes only enough to effect bond breakage without demoting the still excited reducing electron to the ground state of the reduced species. Such processes are envisioned to be most likely in organic species in which there is a minimum of skeletal reorganization after the product leaves the interface.

Of the two possibilities, the former is the least likely to occur. If the surface complex has an electron in an excited state (the intermediate configuration), there are two possible routes for relaxation, as has been seen (c.f. Chapters II and III). One takes the electron back to the electrode (of course, there is the possibility of luminescence here, but it is also unlikely for the same reasons), and the other takes the electron to the ion. Although the lifetimes for the two possible transitions are probably not the same, the chance of luminescence is diminished because of the several decay routes. In addition, this type of luminescence is expected for solvated cationic

species. For these species, it is clear that vibrational factors play an important role in the relaxation process. Especially under driving conditions, which are the conditions one would need to have concentrations of possible luminensing species high enough to see, the vibrational reorientation factors have a large role even though their rates are less than the electronic rates in the overall rate of the reaction. Since there is such a high degree of participation of vibrational motion, it is predicted that pure electronic transitions leading to luminescence stand little chance of being realized. Marcus,[101] however, has indicated that at semiconductor electrodes electroluminescence of a type similar to the direct relaxation process at the electrode may possibly occur.

APPENDIX I

The theory of charge transfer at an electrode presented in this thesis indicates certain similarities between it and the theory of alloys. It is apparent that equation III(30) is expressible in terms of a Green's function solution

$$A_n(\underline{r}_p) = e^{i\underline{k}\cdot\underline{r}_p} + \sum_{q,r} G(\underline{r}_p - \underline{r}_q) \times U_{nn}(\underline{r}_q,\underline{r}_r)\, A_n(\underline{r}_r) . \qquad \text{Al(1)}$$

In Al(1) the Green's function is $G(\underline{r}_p - \underline{r}_q)$ which can, for this case, be expressed as

$$G(\underline{r}_p - \underline{r}_q) = (\Omega/8\pi^3) \int d^3k \, \frac{e^{i\underline{k}\cdot(\underline{r}_p - \underline{r}_q)}}{E - E_n(k)} , \qquad \text{Al(2)}$$

in which Ω is the volume of the atomic cell. The first term, the exponential, appearing on the right in Al(1), represents an incident plane wave. In cases where bound states exist the exponential is zero.[51,53] This is the case investigated by Koster and Slater[49,50] for the impurity site problem, and by Koutecky[44-48] and others for the surface state and chemisorption problem.

By considering the impurity sites in metals as scattering points, and considering the case of the existence of virtual, or resonance states, one realizes the Friedel sum rule. This sum rule is of immense value in analyzing

the self consistent potentials in impurity problems. It is a simple matter to show that the same rule applies to the chemisorption problem (and incidentally to the surface state problem, in cases where the surface states do not exist). The analysis leading to the sum rule for the chemisorption problem follows.[53,102]

The wave equation for the simple scattering problem is given by

$$-\hbar^2/2\mu\nabla^2\phi + V\phi = E\phi, \qquad \text{A1(3)}$$

where μ is the reduced mass. For a spherically symmetric potential V, the general solution of A1(3) is

$$\phi(r,\theta) = \sum_{L=0} R_L(r)P_L(\cos\theta)$$

$$= \sum_{L=0} r^{-1}\chi_L P_L(\cos\theta), \qquad \text{A1(4)}$$

where $P_L(\cos\theta)$ is the Legendre polynomial of the order L. The function χ_L satisfies the separated wave equation

$$d^2\chi_L/dr^2 + \left[k^2 - U(r) - L(L+1)/r^2\right]\chi_L = 0, \qquad \text{A1(5)}$$

where

$$k = (2\mu E/\hbar^2)^{\frac{1}{2}}, \text{ and } U(r) = 2\mu V(r)/\hbar^2 \xrightarrow[r\to\infty]{} 0.$$

The asymptotic forms of the function χ_L are: $\chi_L(r)\to 0$, as $r\to 0$; and as $r\to\infty$

$$\chi_L(r) \longrightarrow (1/2\pi R)^{\frac{1}{2}} \sin(kr + \eta_L(k) + L/2\pi). \quad \text{A1(6)}$$

The phase shift, $\eta_L(k)$, is produced by the perturbing potential. The wavefunction A1(6) is normalized inside a large sphere of radius R.

It is necessary to know the number of particles (e.g., screening electrons) ΔN displaced into a large hemisphere of radius R as a result of the surface potential. First, the change in the number of particles in the state (k,L) is given by

$$2\pi \int_0^R dr \left[\chi_L^2 - (\chi_L^\circ)^2\right] = (1/2R)\left[d\eta_L/dk - (1/k)\sin\eta_L \cos(2kR + \eta_L - L\pi)\right]. \quad \text{A1(7)}$$

The equation A1(7) is obtained by multiplying the wave equation A1(3) by χ_L' and subtracting from it a similar equation for χ_L' multiplied by χ_L. This gives

$$\chi_L'(d^2\chi_L/dr^2) - \chi_L(d^2\chi_L'/dr^2) + (k^2 - k'^2)\chi_L'\chi_L = 0. \quad \text{A1(8)}$$

Integration of this equation over the limits 0 to R gives in the limit as $k' \longrightarrow k$

$$\left[(d\chi_L/dk)(d\chi_L/dr) - \chi_L(d^2\chi_L/dkdr)\right]_0^R = 2k\int_0^R dr\, \chi_L^2 . \quad \text{A1(9)}$$

Evaluating A1(9) for the wavefunction A1(6) and for the wavefunction χ_L^o for the unperturbed case with $\eta_L = 0$ yields A1(7).

The density of states of angular momentum L per unit wavenumber is $2(2L + 1)R/\pi$ inside the sphere of radius R. The total number of particles displaced into the hemisphere of radius R is

$$\Delta N/2 = 1/\pi \sum_L (2L+1) \int_0^{k_F} dk(d\eta_L/dk - (1/k)\sin\eta_L \times \cos(2kR + \eta_L - L\pi)). \qquad A1(10)$$

Neglecting the oscillatory term, the total number above becomes

$$\Delta N = 2/\pi \sum_L (2L + 1)\eta_L(k_F). \qquad A1(11)$$

To insure the self consistency of the potential V(r) screening the impurity perturbation potential at large distances, the displaced charge ΔNe will exactly cancel $Z|e|$, the valence of the impurity. Thus, A1(11) is the Friedel sum rule:

$$Z = 2/\pi \sum_L (2L + 1)\eta_L(k_F). \qquad A1(12)$$

It is now of interest to examine the consequences of the Friedel sum rule applied to electrochemistry.

Let the valence Z be positive. If one of the valence

electrons remains bound to the metal atom it must be lower in energy than the bottom of the band edge. This results simply from the fact that the bound energy states cannot exist in a continuous energy spectrum. If one electron remains bound, then the impurity acts as if it possesses an effective valence Z - 1. Deleting the valence by one on the left of Al(12) requires that the phase shift be deleted by η/π on the right. This means that for consistency the value of the phase shift for the bound state must be π.

It is presumed that for electrochemistry the consequence of the Friedel sum rule is the following. If, for example, positive ions are adsorbed at the electrode surface through their solvation sheath--the sheath assumes an effective positive charge--the binding will involve bound electronic states. Whether there will be additional virtual states, or resonances, with the band system of the metal depends largely upon the number of "effective" valence electrons on the solvate. These bound electronic states account primarily for the binding force at the surface between the surface and the solvated ions. In addition, the bound electrons may be involved in the electronic transitions responsible for the charge transfer as was discussed in Chapter III. It was noted in Chapter IV that energy absorption processes leading to the charge transfer transition in the surface complex can absorb energy from excited states which relax in the metal.

The excited metal states have an associated band structure and consequently a continuous energy spectrum within the width of the band. Hence, there exists the possibility of virtual states resulting from the surface potential, and these states lie in the excited band. The virtual states lead to resonances in which the electrons in the excited band suffer large scattering cross sections. The scattering in the excited band will have an effect on the lifetime of an electron in a state k of that band. Although the scattering is expected to be small, it is of some interest to examine trends that might be expected for it. The smallness of the effect is due to the fact that the scattering is energetically much less than the energy of the interband transitions.

The probability that an electron in the excited band will be scattered and not cause a charge transfer transition in the surface complex is given by $1/\tau$, where τ is the relaxation time.[53] Write

$$1/\tau = n_i \langle I \rangle v, \qquad \text{A1(13)}$$

where n_i is the concentration of scattering centers, $\langle I \rangle$ the average cross section, and v is the velocity of the incident electron equal to $\hbar k/m$. On the basis of A1(13) it is possible to rewrite the expression for the current at an electrode in the following manner. In light of the discussion of the nature of the current due to charge transfer given in Chapter IV, it is easily seen that the

current can be written in the form

$$i_f = NPv = N_o Pv \exp(-E_e/kT), \qquad A1(14)$$

in which N is the number of sites on the surface leading to a current, N_o is the total number of current sites, v is the velocity of the electron, and E_e is the excitation energy necessary to give N. The probability that a charge transfer transition will occur in the surface complex is P. P can be given either by expression IV(17) or IV(99). Equation A1(14) is the current for the zero scattering case. The scattering deletes from the current A1(14) a current

$$i = NPv\langle I\rangle = N_o Pv\langle I\rangle \exp(-E_e/kT). \qquad A1(15)$$

Combining the two currents A1(14) and A1(15) yields A1(16):

$$i_{f(net)} = NP(1 - \langle I\rangle)v = N_o P(1 - \langle I\rangle)v\exp(-E_e/kT). \qquad A1(16)$$

The effective average cross section, $\langle I\rangle$, is given by the expression[53]

$$\langle I\rangle = 2\pi\int_0^{\pi} d\theta \sin\theta\, I(\theta)\,(1 - \cos\theta), \qquad A1(17)$$

where $(1 - \cos\theta)$ is the weighting factor according to the change of k_z, the incident wavenumber. The usual evaluation of the above integral is made in terms of phase shifts (c.f. Mott and Massey[103]). The expression for $I(\theta)$ is

$$I(\theta) = (1/k^2) \left| \sum_{L=0}^{\infty} (2L + 1)\, e^{i\eta_L} \sin \eta_L P_L(\cos \theta) \right|^2 \qquad A1(18)$$

with which A1(17) is evaluated to give (using the orthogonality properties of the Legendre polynomials).

$$(2/k^2) \sum_{L=0}^{\infty} (L + 1) \sin^2(\eta_L - \eta_{L+1}), \qquad A1(19)$$

making use of the relation

$$\sin^2\eta_L - 2\sin\eta_L \sin\eta_{L+1} \cos(\eta_{L+1} - \eta_L)$$

$$+ \sin^2\eta_L = \sin^2(\eta_L - \eta_{L+1}).$$

From the sum rule A1(12) it is found that if only η_L is large then

$$\eta_L = \pi Z/(4L + 2) \qquad A1(20)$$

for which A1(19) reduces to

$$(4\pi/k^2)(L + 1) \sin^2(\pi Z/(4L + 2)). \qquad A1(21)$$

Taking Z = 1 and L = 0, it is seen that $\langle I \rangle$ is of the order of 10^{-15} cm^2. Consequently, the scattering has little effect on the current. However, for the change in resistivity in alloys it is measurable--the change is given by

$$\Delta \rho = (n_i k_F/ne^2) \langle I \rangle . \qquad A1(22)$$

Taking again Z = 1 and L = 0 de Faget de Casteljau and Friedel[104] find that the resistivity is of the order of 4 $\mu\Omega$-cm per percent impurity.

For alloys the velocity is the Fermi velocity taken on the Fermi surface of the band. In the electrochemical problem the Fermi velocity is expected to be fairly low due to the low population of the excited band. It is not, however, the Fermi velocity that is important, rather it is the velocity of the electron having the necessary kinetic energy to excite a surface complex charge transfer transition upon executing a proper collision. In addition, as a result of the low electron density in the band, the electrons in it act as a degenerate electron gas over all wavenumbers of the band. Hence, it is unnecessary to consider an excited Fermi surface, as there is none. The consequences of scattering on the electrochemical current are easy to generalize from the theory of alloys. From the theory of scattering one finds resonances at certain momenta for the incident particles. The dependence of the phase shift and the scattering on momentum is given in Figure 10. Resonances occur at the values of L which correspond to the L value of the energy level of the scatterer. These particles tend to be bound in the virtual level. For alloys the same situation applies. In this case, though, the energy of the incident particles remains fairly constant while the energy of the scatterer varies. This is clearly seen in the reproduction of

Figure 10

The dependence of the phase shift and the scattering on momentum (after Kittel--reference 53--and Merzbacher--reference 105).

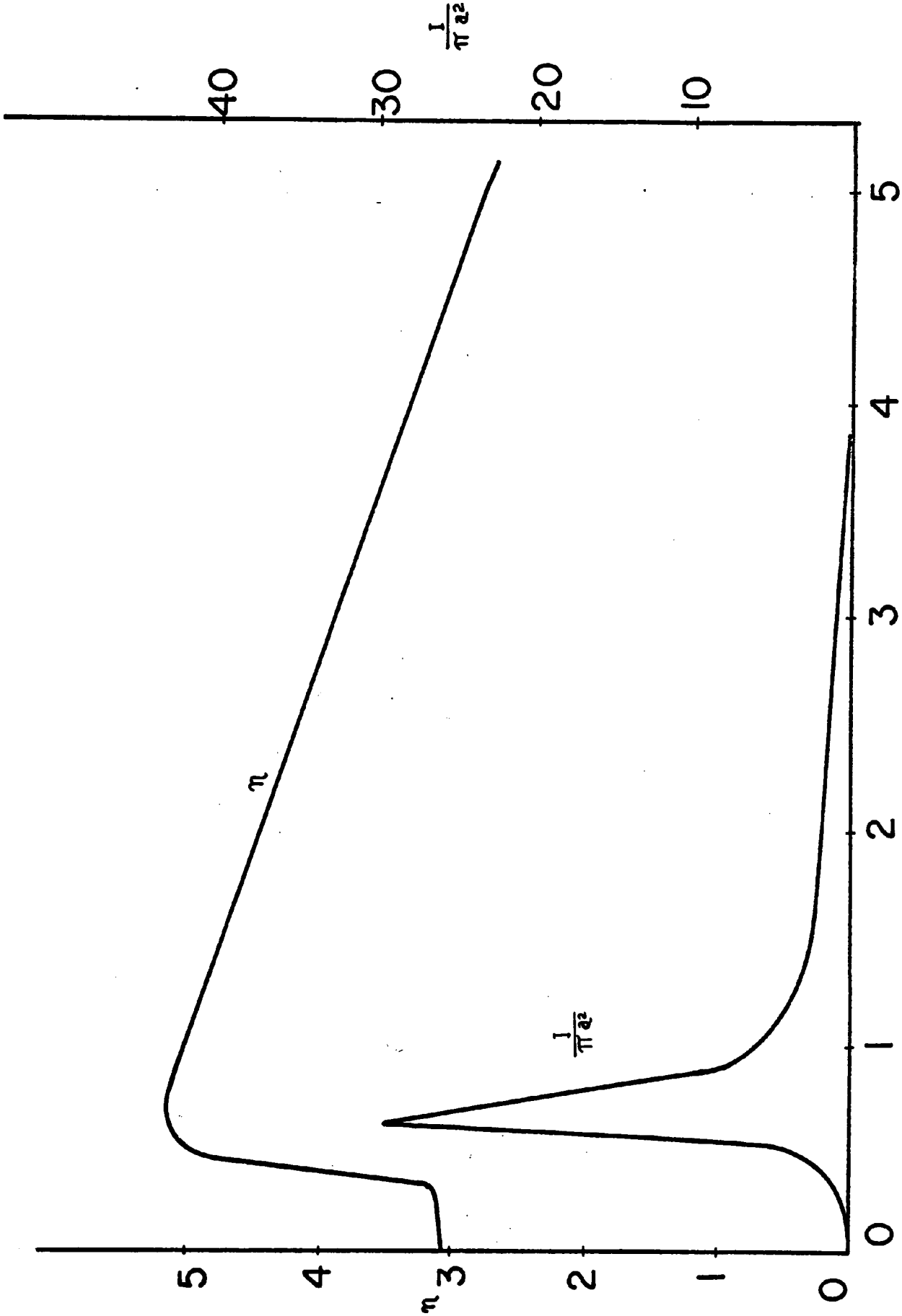


Figure 10

Figure 11

The residual resistivity of aluminum with dissolved transition elements and other impurities (after Friedel--reference 102).

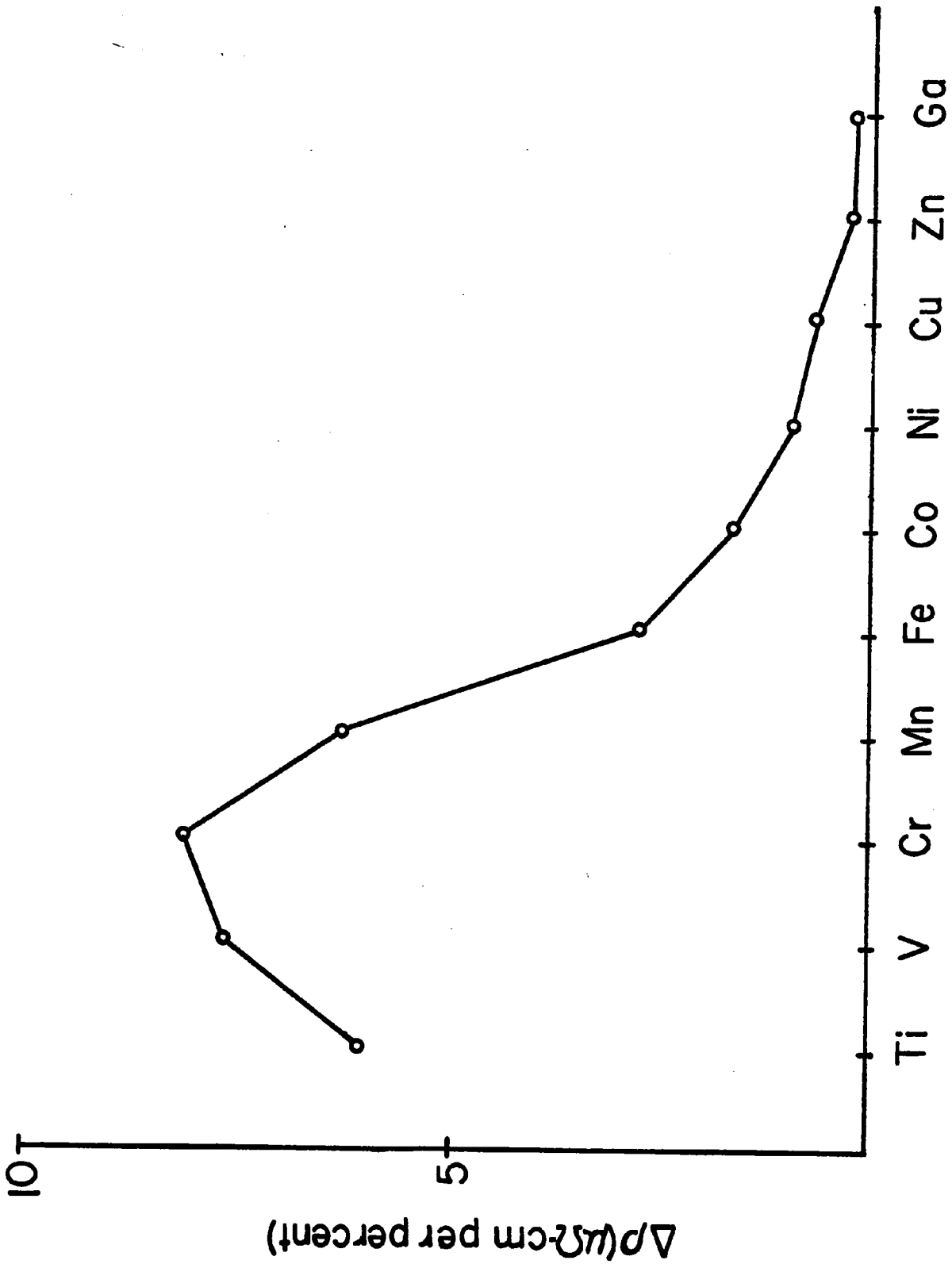


Figure 11

Friedel's data on transition metal impurities in aluminum--c.f. Figure 11. The explanation of the figure is that as one proceeds along the series starting at Ti, bound states below the Fermi surface are filled. At Cr the Fermi surface is crossed, and at this point there is a maximum scattering, hence a resonance maximum.

The electrochemical scattering, however, is not the same. The difference lies in the degenerate electron gas character of the excited band electrons. Given a homologous series, the scattering factor is expected to monotonically increase or decrease depending on the nature of the series. There will be no resonances, as there is no Fermi surface to the band. One may, if one so desires, think of a virtual resonance at ka = 0 if the potential in the series is increasingly negative.

There is one possibility conceivable for the formation of virtual states directly as a result of the chemisorption of electroactive species at the surface. If the solvate were some sort of complex amine or oxy compound having a large percentage of unshared electron pairs in addition to those already coordinated to the central ion core, then it might be possible that enough bound states would be created so that some of the unshared electrons of the ligand would become a part of the conduction band system. This situation corresponds to the formation, in part, of a metallic bond which Grimley[57] has discussed. For such a situation, it is indeed possible that the scattering effect

would make a larger contribution, and thus might be measured. Excitations leading to charge transfer transitions are expected to take place within the solvate-ion system, and the expressions for the electrode current are those given by de Hemptinne[32] and in this work for direct charge transfer.

APPENDIX II

Dyson's proof of the von Laue theorem:[53] Consider the free electron case. The wave equation for a free electron is given by

$$- 1/2m \nabla^2 \phi_k(x) = E_k \phi_k(x) \qquad A2(1)$$

in atomic units. The function $u(x,t)$ is introduced:

$$u(x,t) = \sum_k \phi_k(x)\phi_k(0)\, e^{-E_k t} \qquad A2(2)$$

which at time $t = 0$ is

$$u(x,0) = \sum_k \phi_k(x)\phi_k(0) = \delta(x), \qquad A2(3)$$

and $\delta(x)$ is a Dirac delta function. The function $u(\mathbf{x},t)$ satisfies the diffusion equation:

$$\partial u / \partial t = D \nabla^2 u. \qquad A2(4)$$

This is easily established using A2(1) and A2(2). Using A2(1) and A2(2) in A2(4) shows that the diffusion constant is 1/2m. The Laplace transform of the probability density, $\phi_k(0)\phi_k(0)g(E_k)$, at the origin is

$$u(0,t) = \sum_k \phi_k(0)\phi_k(0)e^{-E_k t}$$

$$= \int dE_k \phi_k(0)\phi_k(0)g(E_k)e^{-E_k t}. \qquad A2(5)$$

At a distance ξ from the origin place a boundary. At a time

t it is seen from the diffusion theory that

$$t > t_c \simeq \xi^2/D = 2m\xi^2. \qquad \text{A2(6)}$$

The above shows that at the time t_c the presence of the boundary is recognized. The greatest contributors to $u(0,t)$ at t_c come from those components for which $E_k t_c < 1$. Using A2(6)

$$E_k < 1/2m\xi^2, \qquad \text{A2(7)}$$

and with $E_k = k^2/2m$

$$k < 1/\xi. \qquad \text{A2(8)}$$

Particles with wavenumbers satisfying A2(8) will experience the effect of the boundary. In terms of the particle wavelength, A2(8) is transformed to

$$\lambda < 1/2\pi\xi. \qquad \text{A2(9)}$$

All particles not satisfying A2(9) will not experience the effect of the boundary; thus the von Laue theorem is proven. The theorem is quite general, and is not restricted to solid ordered systems.

APPENDIX III

We need to see how one proceeds from the familiar form of the Hamiltonian operator to the Hamiltonian in the formalism of second quantization. The Hamiltonian IV(47) is expressed in terms of the density fluctuation operators, consequently the Hamiltonian in terms of creation and annihilation operators is not needed.

The usual representation of the Hamiltonian is

$$H = 1/2m \sum_j p_j^2 + 1/2 \sum_{i,j}' \frac{e^2}{|r_i - r_j|} + v(r) , \qquad A3(1)$$

To find the density fluctuation operators proceed with the Fourier analysis of the Coulomb interaction. This is done simply with the use of the Poisson equation. We can Fourier analyze both the potential and the charge density as follows:[51]

$$V(\underline{r}) = \sum_k V(\underline{k})\, e^{-i\underline{k}\cdot\underline{r}} \qquad A3(2)$$

and

$$\rho(\underline{r}) = \sum_k \rho(\underline{k})\, e^{-i\underline{k}\cdot\underline{r}}. \qquad A3(3)$$

The Poisson equation is

$$\nabla^2 V(\underline{r}) = 4\pi \rho(\underline{r}). \qquad A3(4)$$

Substituting A3(2) and A3(3) into A3(4) gives

$$V(\underline{k}) = -(4\pi/k^2)\rho(\underline{k}). \qquad A3(5)$$

Thus, the potential is written from A3(2) and A3(5)

$$V(\underline{r}) = -4\pi \sum_{k} \rho(k)/k^2 \; e^{-i\underline{k}\cdot\underline{r}}. \qquad A3(6)$$

It is well known that the inverse of a Fourier transform is, for a unit volume,

$$q_k = \int d^3x \; Q(\mathbf{x}) \; e^{i\underline{k}\cdot\underline{x}}. \qquad A3(7)$$

Applying the above relation to the charge density gives

$$\rho(\underline{k}) = \int d^3r \, \rho(\underline{r}) \; e^{i\underline{k}\cdot\underline{r}}. \qquad A3(8)$$

Assume that the charge density is uniform and equal to n: $\rho(\underline{k}) = n\,\delta_{ko}$. For point charges one writes

$$\rho(\underline{r}) = \sum_{j} \delta(\underline{r} - \underline{r}_j) \qquad A3(9)$$

which gives in A3(8)

$$\rho(\underline{k}) = \int d^3r \sum_{j} \delta(\underline{r} - \underline{r}_j) \; e^{i\underline{k}\cdot\underline{r}}$$

$$= \sum_{j} e^{i\underline{k}\cdot\underline{r}_j}. \qquad A3(10)$$

Returning now to A3(6) it follows that

$$V(\underline{r}) = -4\pi \sum_{j,k}{}' \; e^2/k^2 \; e^{i\underline{k}\cdot(\underline{r}_j - \underline{r})}. \qquad A3(11)$$

If, now, in A3(11) instead of $\underline{r}$ we replace it with $\underline{r}_i$ we have the Coulomb interaction potential in terms of its Fourier representation. That is,

$$V(\underline{r}_i - \underline{r}_j) = - \sum_{i,j}{}' \sum_{k} (4\pi e^2/k^2)\, e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)}. \qquad \text{A3(12)}$$

Thus, in terms of the Fourier representation the Hamiltonian A3(1) is transformed into

$$H = 1/2m \sum_{j} p_j^2 + \tfrac{1}{2} \sum_{i,j}{}' \sum_{k\neq 0} (4\pi e^2/k^2) e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)}, \qquad \text{A3(13)}$$

where the positive background, v(r) in A3(1), removes the $\underline{k} = 0$ term. The prime on the i,j, sum excludes the $i = j$ term.

It follows from the discussion concerning the Fourier representation of the Coulomb interaction that for point charges,

$$\rho_k^{+} \rho_k = \sum_{i,j} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)}. \qquad \text{A3(14)}$$

The summation in A3(13) excludes the $i = j$ term. The summation A3(14) less the number of particles becomes the summation in A3(13):

$$\sum_{i,j}{}' e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} = \sum_{i,j} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} - n$$

$$= \rho_k^{+} \rho_k - n. \qquad \text{A3(15)}$$

Replacing the second summation over i,j in A3(13) by A3(15) yields equation IV(47):

$$H = 1/2m \sum_j p_j^2 + \tfrac{1}{2} \sum_{k \neq 0} (4\pi e^2/k^2)(\rho_k^+ \rho_k - n).$$

IV(47)

REFERENCES

1. R. A. Marcus, Ann.Rev. Phys. Chem., 15, 155 (1965) (see references contained therein)

2. H. Gerischer, Z. Physik. Chem. (Frankfurt) 26, 223 (1960); 27, 48 (1961)

3. See, for example, R. Parsons, in Modern Aspects of Electrochemistry, edited by J. O'M. Bockris (Butterworths Scientific Publications Ltd., London, 1954), Vol.1

4. See, for example, J. O'M. Bockris, in Modern Aspects of Electrochemistry, edited by J. O'M. Bockris (Butterworths Scientific Publications Ltd., London, 1954), Vol.1

5. See, for example, P. Delahay, New Instrumental Methods in Electrochemistry (Interscience Publishers, Inc., New York, 1954)

6. N. Sutin, Ann. Rev. Nuclear Sci., 12, 285 (1962)

7. J. Halpern, Quart. Revs. (London), 15, 207 (1961)

8. H. Taube, Advances Inorg. Chem. Radiochem., 1, 1 (1959)

9. H. Gerischer, Ann. Rev. Phys. Chem., 12, 227 (1961)

10. N. Tanaka and R. Tomamushi, Kinetic Parameters of Electrode Reactions, (a report presented to the Commission on Electrochemical Data of the Section of Analytical Chemistry of I.U.P.A.C., at the International Congress of Pure and Applied Chemistry, Montreal, 1961)

11. J. Jordan and N. R. Stalica, Handbook of Analytical Chemistry, edited by L. Meites (McGraw-Hill Book Co., New York, 1963) p.p. 38-46

12. D. R. Stranks, in Modern Coordination Chemistry, edited by J. Lewis and R. G. Wilkins (Intersciece Publishers Inc., New York, 1960) p.p. 148-173

13. K. V. Krishnamutry, Matscience Report 12 (Inst. Math. Sci., Madras India circa 1963)

14. R. A. Marcus, J. Phys. Chem., 67, 853, 2889 (1963)

15. R. W. Gurney, Proc. Roy. Soc.(London) A134, 137 (1931)

16. N. S. Hush, J. Chem. Phys., 28, 962 (1958)

17. N. S. Hush, Z. Elektrochem., 61, 734 (1957)

18. N. S. Hush, Trans. Faraday Soc., 57, 557 (1961)

19. R. A. Marcus, O. N. R. Technical Report No. 12 Project NR 051-331 (1957)

20. R. A. Marcus, Canadian J. Chem., 37, 155 (1959)

21. R. A. Marcus, in Symposium on Electrode Processes, edited by E. Yeager (John Wiley and Sons, Inc. New York, 1961) p. 239

22. R. A. Marcus, J. Chem. Phys., 43, 679 (1965)

23. R. R. Dogonadze and Y. A. Chizmadzhev, Proc. Acad. Sci. USSR, Phys Chem Sect., 144, 463 (1962)

24. R. R. Dogonadze and Y. A. Chizmadzhev, Proc. Acad. Sci. USSR, Phys. Chem. Sect., 145, 563 (1962)

25. V. G. Levich and R. R. Dogonadze, Proc. Acad. Sci. USSR, Phys. Chem. Sect., 124, 9 (1959)

26. V. G. Levich and R. R. Dogonadze, Proc. Acad. Sci. USSR, Phys. Chem. Sect., 133, 591 (1960)

27. V. G. Levich and R. R. Dogonadze, Coll. Czech. Chem. Comm., 26, 193 (1961)

28. R. R. Dogonadze, Proc. Acad. Sci. USSR, Phys. Chem. Sect., 142, 156 (1961)

29. R. A. Marcus, J. Chem. Phys., 24, 966 (1956)

30. R. A. Marcus, Discussions Faraday Soc., 29, 32 (1960)

31. R. A. Marcus, private communication

32. X. de Hemptinne, Bull. Soc. Chim. France, 2328 (1964)

33. P. P. Schmidt, Jr., and H. B. Mark, Jr., J. Chem. Phys., 43, 3291 (1965)

34. J. Hale, J. Electroanal. Chem., 11, 154 (1966)

35. H. B. Mark, Jr., J. Electrochem. Soc., 7, 276 (1964)

36. H. B. Mark, Jr., J. Electrochem. Soc., 8, 253 (1964)

37. H. B. Mark, Jr., and C. N. Reilley, Anal. Chem., 35, 195 (1963)

38. D. A. Aikens, and J. W. Ross, Jr., J. Phys. Chem., 65, 1213 (1961)

39. J. G. Jones, and F. C. Anson, Anal. Chem., 36, 1137 (1964)

40. S. L. Phillips, Div. of Anal. Chem. 149th ACS Meeting Detriot, Michigan, April, 1965

41. M. Heyrovský, Nature, 206, 1356 (1965)

42. M. Heyrovský, private communication

43. R. S. Mulliken, J. Am. Chem. Soc., 74, 811 (1953)

44. J. Koutecký, Coll. Czech. Chem. Comm.,22, 683 (1957)

45. J. Koutecký, Coll. Czech. Chem. Comm., 22, 669 (1957)

46. J. Koutecký, Trans. Faraday Soc., 54, 1038 (1958)

47. J. Koutecký, and A. Fingerland, Dokl. Akad. Nauk SSSR, 125, 841 (1959)

48. J. Koutecký, and A. Fingerland, Coll. Czech. Chem. Comm., 25, 1 (1960)

49. G. Koster, and J. C. Slater, Phys. Rev., 95, 1167 (1954)

50. G. F. Koster, and J. C. Slater, Phys. Rev., 96, 1208 (1954)

51. J. Callaway, Energy Band Theory, (Academic Press, Inc. New York, 1964)

52. A. Wolff, Phys. Rev., 124, 1030 (1961)

53. C. Kittel, Quantum Theory of Solids, (John Wiley and Sons, Inc., New York, 1963)

54. J. Koutecký, Phys. Rev., 108, 13 (1957)

55. G. R. Baldock, Proc. Camb. Phil. Soc., 48, 457 (1952)

56. J. Koutecký, in Advances in Chemical Physics, (John Wiley and Sons, New York, 1965) Vol. IX, p.p.85-168

57. T. B. Grimley, Proc. Phys. Soc. (London), B72, 103 (1958)

58. I. Tamm, Z. Physik., 76, 849 (1932)

59. W. Shockley, Phys. Rev., 56, 317 (1939)

60. J. N. Murrell, and H. C. Longuet-Higgins, Proc. Phys. Soc. (London), A68, 81 (1955)

61. H. Eyring, J. Walter, and G. E. Kimgall, Quantum Chemistry, (John Wiley and Sons, Inc., New York, 1944)

62. T. M. Dunn, unpublished notes on Molecular Field Theory

63. C. J. Ballhausen, and H. B. Gray, Molecular Orbital Theory, (W. A. Benjamin, Inc., New York, 1964)p.p.92-95

64. J. N. Murrell, Quart. Revs. (London), 191 (1961)

65. H. C. Longuet-Higgins, and J. N. Murrell, Proc. Phys. Soc. (London), A68, 601 (1955)

66. J. A. Pople, Proc. Phys. Soc. (London), A68, 81 (1955)

67. J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953)

68. J. Halpern, and L. E. Orgel, Discussions Faraday Soc., 29, 32 (1960)

69. L. I. Schiff, Quantum Mechanics, (McGraw-Hill Book Co., Inc., New York, 1955, Second Edition)

70. J. C. Slater, Quantum Theory of Matter, (McGraw-Hill Book Co., Inc., New York, 1951)

71. L. D. Landau and E. M. Lifshitz, Quantum Mechanics--Non-Relativistic Theory, (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958)

72. G. W. Robinson, and R. P. Frosch, J. Chem. Phys., 37, 1962 (1962)

73. G. W. Robinson, and R. P. Frosch, J. Chem. Phys., 38, 1187 (1963)

74. M. Gouterman, J. Chem. Phys., 36, 2846 (1962)

75. P. P. Schmidt, Jr., and H. B. Mark, Jr., J. Chem. Phys., to be published

76. W. T. Simpson, J. Am. Chem. Soc., 73, 5363 (1951)

77. D. Pines, Elementary Excitations in Solids, (W. A. Benjamin, Inc., New York, 1963)

78. P. Nozières,and D. Pines, Nuovo Cimento, [X]9, 470 (1958)

79. P. Nozières, and D. Pines, Phys. Rev., 109, 741, 762 1062 (1958)

80. D. L. Dexter, J. Chem. Phys., 21, 836 (1953)

81. D. P. Craig, and S. H. Walmsley, Mol. Phys. 4, 113 (1961)

82. S. W. Benson, The Foundations of Chemical Kinetics, (McGraw-Hill Book Co.,Inc., New York, 1960) p.p. 161-167

83. H. A. Bethe, Intermediate Quantum Mechanics, (W. A. Benjamin, Inc., New York, 1964)

84. A. Frumkin, in Trans. Symp. Electrode Processes, edited by E. Yeager, (John Wiley and Sons, Inc., New York, 1961)p. 1

85. D. C. Grahame, A. E. Higinbotham, and F. R. M. Deane, in Trans. Symp. Electrode Processes, edited by E. Yeager (John Wiley and Sons, Inc., New York, 1961) p.197

86. J. Llopis, J. Fernandez-Biarge, and M. Perez-Fernandez, in Trans. Symp. Electrode Processes, edited by E. Yeager (John Wiley and Sons, Inc., New York, 1961).p. 221

87. P. Delahay, in Trans. Symp. Electrode Processes, edited by E. Yeager, (John Wiley and Sons, Inc., New York, 1961) p. 291

88. P. Delahay, Double Layer and Electrode Kinetics, (John Wiley and sons, Inc., New York, 1965) p. 291

89. J. O'M. Bockris and D. A. J. Swinkels, J. Electrochem. Soc., 111, 736 (1964)

90. J. O'M. Bockris, and D. A. J. Swinkels, J. Electrochem. Soc., 111, 743 (1964)

91. J. O'M. Bockris, M. A. V. Devanthan, and K. Müller, Proc. Roy. Soc., A247, 55 (1963)

92. R. Suhrmann, in Adv. in Catalysis, VII, 345 (1955)

93. J. C. P. Mignolet, in Chemisorption, edited by W. E. Garner, (Butterworths Scientific Publications Ltd., London, 1957) p. 123

94. R. L. Flurry, J. Phys. Chem., 69, 1927 (1965)

95. R. L. Flurry, Div. of Phys. Chem., 150th ACS Meeting, Atlantic City, New Jersey, Sept., 1965

96. S. M. Blinder, unpublished lecture notes, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan

97. H. B. Mark, Jr., and B. S. Pons, Anal. Chem., 38, 119 (1966)

98. R. Piontilli, G. Poli, and G. Serravalle, Trans. Symp.

Electrode Processes, edited by E. Yeager, (John Wiley and Sons, Inc., New York, 1961)

99. See, for example, L. Gierst, Symposium of Electrode Processes of the Theoretical Division, Spring Meeting of The Electrochemical Society, Inc., Cleveland, Ohio May 1966

100. R. W. Gurney, Ionic Processes in Solution, (McGraw-Hill Book Co., Inc., New York, 1953) c.f. Chapters 10, 11 and 16

101. R. A. Marcus, J. Chem. Phys., 43, 2654 (1965)

102. J. Friedel, Nuovo Cimento supplimento, 7, 287 (1958)

103. N. F. Mott, and H. S. W. Massey, The Theory of Atomic Collisions, (Oxford University Press, London, Second Edition, 1949)

104. P. de Faget de Casteljau, and J. Friedel, J. Phys. Radium, 17, 27 (1956)

105. E. Merzbacher, Quantum Mechanics, (John Wiley and Sons, Inc., New York, 1961) p. 236