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KINETICS OF CHARGE TRANSFER AT METAL ELECTROLYTE INTERFACES: FROM CLASSICAL TO QUANTUM STATISTICS

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ABSTRACT

A survey of recent developments in the theory and experimental knowledge of the charged interfaces are discussed in relation to the problem of electron transfer reactions. An attempt is made to reformulate the role of the solvent in bulk phase and at surfaces. Furthermore we discuss the effect of position dependent tunneling on the reaction rate constant assuming simple distribution of the ions near the metallic interface.
INTRODUCTION

The understanding of the chemical reactions occurring at electrodes, batteries or electrochemical cells, corrosion and membrane function are still open problems when we consider the mechanism from a first principles point of view. Perhaps the earliest attempt to explain the mechanism of inhomogeneous electron transfer is due to Gurney (1931). In this work the basis of the modern theory was laid, and a formal expression for the rate of the reaction (the current intensity) is given in terms of the quantum mechanical transition probability at the electrode interface and the spatial distribution of both ions and electrons on both sides of the interface. Assume that we have the electron transfer reaction between species A and B. A could be the metal phase, or also an atom or molecule. The electron transfer reaction is schematically

\[ A + B \rightarrow A + B^- \]  \hspace{1cm} (1)

For this reaction the rate is

\[ k = \iiint_{\Gamma} P_N f(\theta) \, d\theta \, dx \]  \hspace{1cm} (2)

where \( P_N \) is the transition probability, which is a function of the position of the ion relative to the surface, and also the id\( \text{nic} \)
Concentration at that position $o(x)$

$$P = \rho_B(x) \chi(\theta, x)$$  \hspace{1cm} (3)

where $\rho_B(x)$ is the density of species $B$ and $\chi(\theta, x)$ is the reaction probability for the transfer process. It can be computed for simple models such as, for example in the electrode case, the square or triangular barrier. In our calculations we have assumed that the width of the barrier depends on $x$. The interesting point about this quantity is that with the advent of the scanning tunneling microscope (STM), direct measurements of this quantity is possible. In (2) $N(\theta)$ is the density of states for energy $\theta$, the occupancy of these levels by the electrons in the metal is given by the Fermi-Dirac distribution function $f(\theta)$. The more detailed analysis of this theory by Gerischer [2] also points to the importance of the solvent in the process of electron transfer from an ion to the metallic phase.

Clearly in a model of this kind the transition probability, which in fact is a tunneling probability has to be modelled in some simple way (Gerischer used a square barrier) and the parameters of the model must be guessed in a reasonable way. The fact is that in a real system there will be a large number of different configurations that will lead to significant probability of electron transfer, and the total rate will be a statistical average, in some sense, of the individual probabilities that correspond to specific geometrical arrangements of the surface atoms and of the solvent molecules. If we pretended to include all the atoms and molecules involved in this process, we would get, very quickly, into an impossible problem, even for the largest available computer.
Therefore there is a clear need for a statistical theory in which the random nature of the system is taken into account. This is the basic concept behind the popular theory of Marcus [3], and also is well discussed in a recent paper by Hynes [4]. We must remark that these are more general theories which also include the electron transfer reactions in bulk phase.

The point in these theories is that out of the manifold of coordinates that are involved in the electron transfer process, there is one, $\lambda$, that is the reaction coordinate, which plays the most important role, and which determines the extent of the reaction. For example, if we are talking of the transfer of electrons between an atom A and an atom B, then, if we write for our total wave function the linear superposition

$$\psi = \lambda \left[ \psi_A \cdot \psi_B \right] + (1-\lambda) \left[ \psi_A \psi_B^- \right] \quad (4)$$

the parameter $\lambda$ will indicate the extent of the reaction. There will be, in general, an energy barrier between the initial and final states of the system. The analysis of the system in the configuration of maximum energy, the activated state in terms of partition functions, has led to absolute rate theory. More recent work has stressed stochastic models such as that of Kramers [5] (see for example the work of Hynes [4] and references cited therein). The first observation is that if we want to construct a model the activated state of the electron transfer in the interface of a metal and a solution we need to know the structure of the initial and final states, at the very least. We would like to discuss
some of the recent theoretical and also experimental developments in this area in the next section of this article. The next observation is that we want to construct a first principles theory, and that necessarily involves an average of the reaction probabilities, or cross sections for every given configuration of the surrounding solvent molecules. In other words, we have to construct a manifold of solutions of Schroedinger's equation for every solvent configuration, and calculate the cross sections [6,7], which may involve such interesting features as resonances. This presents itself as an almost impossible task. A more sensible route is to use the transition state theory, which still gives a simple recipe for the transition probabilities, for every solvent configuration, and then average the rate constants. For example, one could use Monte Carlo sampling techniques (8,9,10), and then sample the solvent configurations in the usual manner. This approach has been used in solution reactions where fairly reliable models of the solvent and solute are available. However the problem here is that this may be OK for bulk reactions, but to date, there is no computer simulation of an ionic type solution near a charged interface, that is we are again back to the structural problem of the molecular solution. Our proposal here is that it is possible, using simple models of the solvent, like the ion dipole model[11], to obtain a representation as accurate as possible of the thermodynamics and structure functions. Then, we can compute the local, fluctuating electric microfield using either a Monte Carlo or molecular dynamics method, and also, integral equations such as the hypernetted chain (HNC) equation or the modified HNC [12] which are known to be fairly accurate equations for bulk systems [13]. The advantage of this approach is that it can be extended to the interface case in a more or less straightforward way [14]. But again, this assumes that we have a
good idea of the structure of a metal-electrolyte interface. To formulate the problem in more precise terms, assume that the system of our two atoms A (eventually, A could be the metal electrode!) and B undergoing the electron exchange reaction

\[ A + B = A + B^- \quad (1) \]

Assume now that we have computed the reaction probability \( \mathcal{X}(\mathbf{E}, x) \) as a function of the external applied field \( \mathbf{E} \). Then, the overall average reaction rate \( k \) is given by

\[ k = \int d\mathbf{E} \int dx \int d\mathbf{E}^* W(\mathbf{E}, x) \mathcal{X}(\mathbf{E}, \mathbf{E}^*, x) \rho(x) N(e) f(e) \quad (5) \]

where \( W(\mathbf{E}, x) \) is the probability of having a local electric field \( \mathbf{E} \) at position \( x \). Now the distribution function \( W(\mathbf{E}, x) \) is also a function of the voltage bias in the case of an electrode. The detailed theory for this quantity in the case of the ion dipole mixture will be discussed elsewhere. Let us now review the situation with respect to \( \rho(x) \).

**STRUCTURE OF THE INTERFACE**

There is very little hard experimental evidence for the actual structure of the charged interface, when it is active, that is when current is flowing (in situ). Only very recently have experiments been reported in which a direct measurement of the surface structure has been made \([15],[16]\). In both experiments the basic
principle is to deposit selectively a monolayer of an atomic species on the surface, and then use a resonance technique to isolate the signal coming from the surface atoms. A total of three fluorescence EXAFS experiments were done: In the first one, iodine on platinum, very little signal was detected, but this may be just a consequence of experimental problems. For Cu on gold, a clear signal coming from the Cu-O distance was seen. There is an open question in this experiment: why does the underlying gold give little or no contribution to the spectra. One possibility is a large Debye Waller factor or also a degree of disorder of the copper atoms in the monolayer. The third reported experiment was of Pb on silver: again the EXAFS spectra indicates strongly bound oxygen, and absolutely no contribution from the Pb-Ag bond. In this case, however, recent in plane surface diffraction experiments [17] by Melroy and collaborators shows the reason of why this is so. The lead forms an incommensurate layer on top of the gold. This incommensurate monolayer is slightly misaligned with the silver crystal. Therefore there is a wide distribution of distances that wipes out completely the silver-lead signal. There are a large number of ex-situ experiments, in which the surface of the metal is analyzed before and after electrochemical reactions have been performed on it. But by and large, our knowledge of the ionic distribution is based largely on theory and its comparison to computer experiments. Although there exist quite realistic models of potentials for water, it has been impossible to simulate with them an electrode interface. Actually there are no reliable simulations for the simple ion-dipole model near a charged interface to date. Therefore, the road to obtaining reliable information about this simplified model has been based on a number of approaches: First, one tries to develop a reliable equation for the so-called primitive model,
in which the solvent is a continuum dielectric, and which has been simulated extensively [18] by Valleau and co-workers. In our opinion, this is a well understood model, at least for sufficiently low density and electric charge on the wall. The case of the ion dipole model near a flat wall has been discussed theoretically, and the best we can do at least for the time being is to solve the so-called GMSA/LHNC equation [14]. The interesting features of this model are the fact that the solvent and the ions form a layered structure near the interface. This also induces an oscillatory profile in the polarization density and hence, also in the local electric field. We should remark that in these models the metal side is treated as a smooth, rigid hard wall. Therefore, the transfer of charge is not permitted. This also holds true for the so-called jellium model [19], in which the metal side is treated as a quantum system using the density functional theory of Kohn and coworkers. A treatment of a conducting interface shows that one can maintain a potential bias only if the interface is ideally impermeable (does not exist in nature) or by passing a current.
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