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Conference Paper

Quantum Statistical Aspects of Charge Transfer on Electrodes*

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Here we present a new attempt to treat the problem of charge transfer on metal electrodes using the new techniques of quantum statistical mechanics. Making some of the assumptions which are common in chemical kinetics we obtain a simple generalization of the linear response theory. When this result is applied to the charge transfer, it leads to a current-overpotential relation differing qualitatively from the prediction of the absolute reaction rate theory. A comparison of the two for some standard reactions seems to favor our prediction.

There exist many applications of quantum statistical mechanics to chemical kinetics, but to our knowledge a paper of Grafov[1] is the only application to electrode kinetics. Grafov used essentially the linear response theory and therefore was limited to low overpotentials. We have developed a nonlinear theory and with its help were able to develop a treatment for the usual range of overpotentials. In this paper, after briefly sketching the basic principles of this new theory, we will discuss its consequence for heterogeneous charge transfer.

We start from the exact Liouville-von Neumann equation for a N-electron-system

$$i\hbar \frac{d\varrho(t)}{dt} = [H, \varrho(t)] = H^{*}\varrho(t), \tag{1}$$

$$H = H_0 + A(t) = H_0 + E(t) \sum_{j=1}^{N} e_j r_j$$

where ϱ stands for the N-electron density matrix, H_0 represents the complete Hamiltonian of the interface at the potential of zero current. It depends in a parametric way on the coordinates of the ions and solvent molecules. A is the perturbation caused by a static electric field E. The r'_js are simply the distances of the electrons from the metal surface. Since we are dealing with an open system we use a grand canonical ensemble. Thus at equilibrium

$$\varrho(-\infty) = Z^{-1} e^{-\beta(H_0 - \mu N)} \tag{2}$$

where Z is the partition function of the grand canonical ensemble and μ the chemical potential.

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The expectation value of the current is given by

$$< J > = \mathrm{Tr} J \varrho. \tag{3}$$

To compute it we introduce, following Zwanzig[2], projection operators which split ϱ into two parts.

$$P \varrho = f \quad \text{and} \quad (1 - P) \varrho = P' \varrho = g. \tag{4}$$

f should represent the part of the density matrix responsible for the current, so that we have the following relations

$$\mathrm{Tr} J f = < J > \quad \text{and} \quad \mathrm{Tr} J g = 0.$$

These two formula's are in fact the definitions of P and P′. When we apply these two projections operators on the Liouville-von Neumann equation, we get two coupled equations for f and g

$$i\hbar \frac{df(t)}{dt} = PH^* f(t) + PH^* g(t) \tag{5}$$

and

$$i\hbar \frac{dg(t)}{dt} = P'H^* f(t) + P'H^* g(t), \tag{6}$$

with the boundary conditions

$$g(-\infty) = \varrho(-\infty) \tag{7}$$

and

$$f(-\infty) = 0. \tag{8}$$

As long as the current is not extremely high, f will be very much smaller than g

$$f(t) \ll g(t). \tag{9}$$

We can therefore neglect the term proportional to f in the second equation. Now after the application of the field our system is again in a stationary state and we have as a solution of the second equation

$$g_0 = Z^{-1} e^{-\beta (P'H - \mu N)}. \tag{10}$$

Now since A is proportional to the number operator, we know that we must renormalize our Hamiltonian. If we assume that the energy spectrum of $P'H$ is the same as that of H_0, this simply gives the number operator multiplied by a constant. So

$$g = Z^{-1} e^{-\beta [H_0 - (c + \mu) N]}. \tag{11}$$

The renormalized chemical potential

$$\breve{\mu} = c + \mu \tag{12}$$

is simply the electrochemical potential. Naturally, this approximation is only the first step of a detailed self-consistent Hartree-Fock treatment to determine the value of c. First attempts in this direction were made by P. Drossbach[3] and co-workers.

Now since f is small, we can further neglect the term $P A^* f$ in the first equation and solve it formally. After some standard manipulations we get

$$f = \frac{1}{i\hbar} Z^{-1} \int_0^\infty \exp\left(-i \frac{H_o^{*}}{\hbar} t\right) PA^* \exp[-\beta (H_0 - \breve{\mu} N)]\, dt \tag{13}$$

We use this result and a formula of Kubo

$$[A, e^{-\beta(H_0 - \breve{\mu}N)}] = -i\hbar E e^{-\beta(H_0 - \breve{\mu}N)} \int_0^\beta J(-i\hbar\lambda)\, d\lambda \tag{14}$$

to compute the expectation value of the current. We then get the following result

$$< J > = - Z^{-1} E \mathrm{Tr} \int_0^\beta J(\tau)\, d\tau P e^{-\beta(H_0 - \breve{\mu}N)} \int_0^\infty J(-i\hbar\lambda)\, d\lambda \tag{15}$$

We now turn back to the interface and consider the passage of electrons from ions in the OHP to the metal or *vice-versa.* We take the case in which only those electrons can pass whose energy is higher than a certain limit $\varepsilon^{\neq}$ [4]. Then P becomes a product of two operators

$$P = T\breve{P} \tag{16}$$

$\breve{P}$ is defined as before and T as follows

$$\begin{aligned} T\,|\,i> &= 0 \quad \text{if} \quad \varepsilon_i < \varepsilon^{\neq} \\ T\,|\,i> &= |\,i> \quad \text{if} \quad \varepsilon_i \geqslant \varepsilon^{\neq} \end{aligned} \tag{17}$$

So T is the projection on the orthonormal set of the first m eigenstates which do not fulfill the second condition. With this definition of P we can further evaluate our formula. We also make the one-electron approximation and by this neglect all possible collective effects. So we get

$$< J > = - E \sum_{i=m}^{\infty} (e^{\beta(\varepsilon_i - \breve{\mu})} + 1)^{-1} < i \,|\int_0^\beta J(-i\hbar\lambda)\, d\lambda \int_0^\infty J(\tau)\, d\tau \,|\, i > \tag{18}$$

The i's design again the eigenstates of our system. We further assume that

$$\varepsilon_m - \breve{\mu} \ll kT \tag{19}$$

and we insert for $\breve{\mu}$[5]

$$\breve{\mu} = \mu_e^o + \alpha e(\varphi_2 - \varphi_M^o) + \alpha e\eta \tag{20}$$

in the notation of Delahays' book. α is an average quantity and absorbs in the usual global way a large part of the double-layer theory. Also we put

$$E = \frac{\eta}{x}, \tag{21}$$

where we assume that in the space between metal surface and OHP the ideal condenser approximation holds. Inserting this we obtain finally for the current

$$< J > = - \frac{\eta}{x} e^{\beta(\mu_e^o + \alpha e(\varphi_2 - \varphi_M^o))} e^{-\beta\alpha e\eta} \sum_{i=m}^{\infty} e^{-\beta\varepsilon_i} < i \,|\int_0^\beta J(-i\hbar\lambda)\, d\lambda \int_0^\infty d\tau J(\tau) \,|\, i > \tag{22}$$

If we combine all the η independent factors into a constant σ, this becomes

$$i = \eta \sigma e^{-\frac{\alpha e \eta}{kT}} \tag{23}$$

This result differs markedly from the result of absolute reaction rate like treatments, the Butler-Volmer equation. The difference arises from the different treatment of external driving forces in the absolute reaction rate theory, which does not seem to be valid in this case. We have looked at several experimental results, some examples of which are shown in the figures. In Fig. 1 we compare the two best fittings in the usual logarithmic plot. However, in order to show the validity of (23) it is more natural to plot

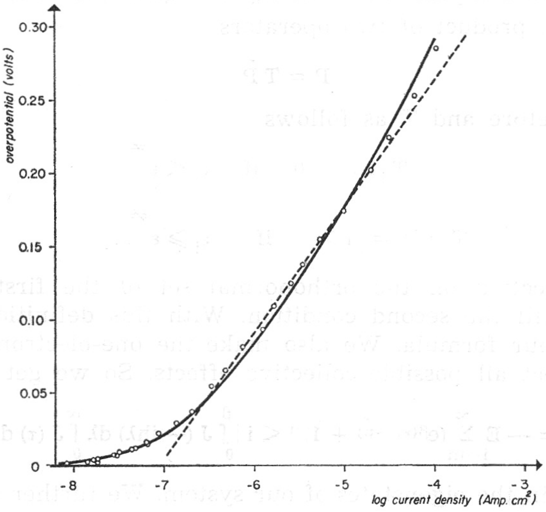

Fig. 1. Comparison of the prediction of the present theory (bold line) with Tafel's law (broken line) for the h. e. r. on Ni in alkaline solution (0.005 *N* NaOH at 3⁰ C). Experimental points[6]

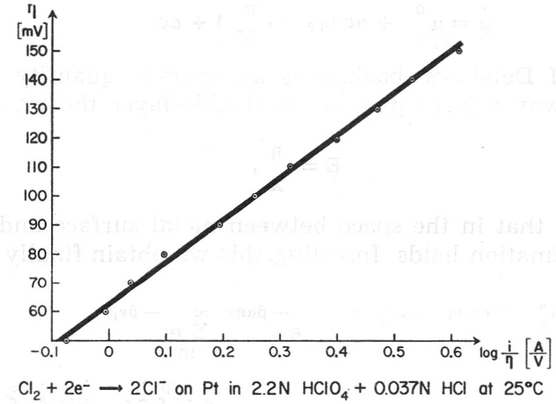

Fig. 2. Cl_2-ionization on Pt-Pt in 2.2 *N* $HClO_4$ + 0.037 *N* HCl at 25⁰ C[7].

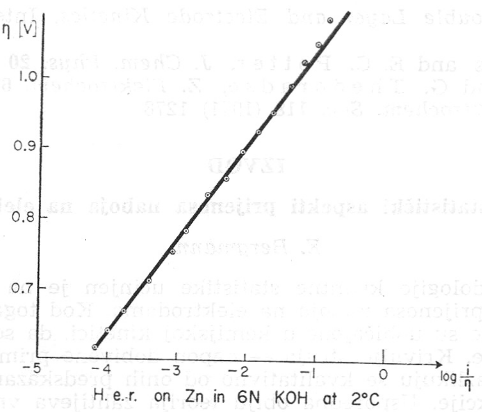

Fig. 3. H. e. r. on Zn in 6 *N* KOH at 2⁰ C[8].

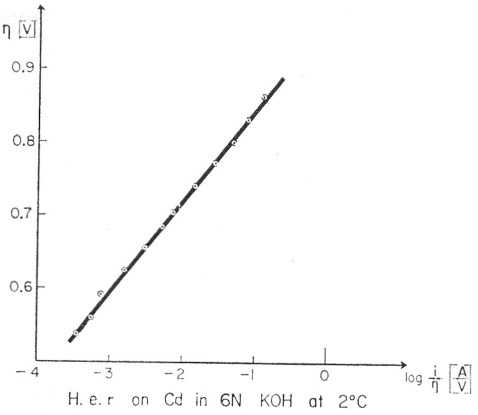

Fig. 4. H. e. r. on Cd in 6 *N* KOH, at 2⁰ C[8].

$\log \frac{i}{\eta} \leftrightarrow \eta$. This should give a straight line, if (23) holds. Obviously the agreement is very satisfactory but the difference could only be shown in a conclusive way by very precise measurements which we think are strongly needed. However, the present approach has the advantage of starting from completely rigourous first principle equations. All the assumptions made in the derivation of the final result are explicitely stated. So they can be criticized and improved very easily. We have mentioned some examples.

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REFERENCES

1. B. M. Grafov, *Elektrokhimiya* **4 (1968) 50.**
2. R. Zwanzig, *Lectures in Theoretical Physics,* Boulder, 1960, vol. 3.
3. P. Drossbach and P. Schmittinger, *Z. Naturforsch.* **25a (1970) 823.**
4. J. O'M. Bockris and N. Mathews, *Modern Electrochemistry,* Vol. 6. Plenum Press, New York, 1970.

5. P. Delahay, *Double Layer and Electrode Kinetics,* Interscience Publishers, New York, 1965.
6. J. O'M. Bockris and E. C. Potter, *J. Chem. Phys.* **20** (1952) 614.
7. A. Frumkin and G. Thedoradse, *Z. Elektrochem.* **62** (1958) 251.
8. T. S. Lee, *J. Electrochem. Soc.* **118** (1971) 1278.

IZVOD

Kvantno-statistički aspekti prijenosa naboja na elektrodama

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Primjenom metodologije kvantne statistike učinjen je na novi način pokušaj tumačenja problema prijenosa naboja na elektrodama. Kod toga treba izvršiti samo one pretpostavke, koje su uobičajene u kemijskoj kinetici, da se dobiju jednostavne linearne generalizacije. Krivulje struja — napon dobivene primjenom ovih kvantno statističkih relacija razlikuju se kvalitativno od onih predskazanih teorijom o apsolutnim brzinama reakcije. Usporedba obiju teorija zahtijeva vrlo precizne eksperimentalne podatke.

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