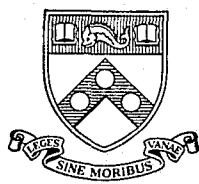


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UNIVERSITY OF PENNSYLVANIA
 DEPARTMENT OF CHEMISTRY
 PHILADELPHIA, PENNSYLVANIA 19104

(NASA-CR-143378) FUNDAMENTAL STUDIES
 CONNECTED WITH ELECTRO-CHEMICAL ENERGY
 STORAGE Final Report (Pennsylvania Univ.)
 194 p HC \$7.00 CSDL 10A

N75-30647

Unclas
G3/44 32910

UNIVERSITY OF PENNSYLVANIA

FINAL REPORT ON:

FUNDAMENTAL STUDIES CONNECTED WITH
ELECTROCHEMICAL ENERGY STORAGE

N.A.S.A. GRANT

NO. N.G.L. 39-010-002.

WORKERS: E. BUCK

R. SEN

DIRECTOR: J.O'M. BOCKRIS

LOCALE OF WORK: Department of Chemistry,
University of Pennsylvania,
Philadelphia, PA.

RPP

February 6, 1974

Dr. John O'M. Bockris
Flinders University
Bedford Park, S. A. 5042
Australia

Dear John:

Your bulky letter of December 7, 1973, reached me on February 5, 1974, probably by sailboat from Australia. Anyhow, I am delighted to receive the somewhat late, final report on NSA 39-01C-002, consisting of a paper by Dr. Buck and series of papers by Mr. Sen. Let me know, please, to which journals these have been submitted; or the reference, if already published. Since it is not clear to me what, if any, distribution you are making of this report, I am sending my copy to our office of Scientific and Technical Information, to be listed in STAR and treated as the reproducible copy for filling requests and for producing microcopy.

You will be pleased to learn that Industry Week of February 4, announces that Australia's Coal and Allied Industries Ltd. has just sold 200,000 tons of NSW steaming coal to the East Coast of the US.

Sincerely yours,

Ernst M. Cohn
Manager, Solar and
Chemical Power

bccs:

cc:

KS/Scientific & Tec. Info. Ofc./w. enc
P/ofc. University Affairs
DHC/Headquarters Contract

GENERAL DESCRIPTION OF WORK, ETC.

The work described concerns the last period of electrochemical research carried out for N.A.S.A. in the Electrochemistry Laboratory. To gain perspective, it is stated that, over the ten years of continuous support of N.A.S.A. to the Electrochemistry Laboratory, the basis governing the direction of the work was N.A.S.A.'s interest in electrochemical energy conversion, i.e., in fuel cells. For this reason, much of the work published earlier in the decade was with respect to topics such as the potential of zero charge, electrocatalysis, and porous electrode theory. From 1968, the emphasis in the work changed, as a consequence of the technological success of N.A.S.A.'s fuel cell efforts. The new emphasis went onto electrochemical energy storage devices. However, in keeping with all the work supported by N.A.S.A. in the Electrochemistry Laboratory, work done was entirely fundamental in character.

WORK OF DR. E. BUCK

ADSORPTION OF DENDRITE INHIBITORS ON ZINC

INTRODUCTION

The formation of dendritic zinc is a major obstacle hindering the attainment of optimum efficiency in alkaline zinc batteries. Previous work¹ in this laboratory has showed the efficacy of quaternary amines in inhibiting the growth of zinc dendrites during the charging cycle in alkaline zincate solutions. Dendritic growth occurs during the charging cycle at cathodic overpotentials greater than 70 millivolts.

In order to most effectively exploit the observation that some quaternary amines inhibit zinc dendrite growth, it is necessary to understand the parameters governing the adsorption of various quaternary amines on a solid zinc electrode. These parameters are, in general, obtainable from electrocapillary data. Unfortunately however, zinc is not an ideally polarizable electrode; consequently electrocapillary data is or even pseudo-electrocapillary data is experimentally unobtainable.

Since the thermodynamic quantities (surface excesses, etc.) are not available to us, the only alternative is to measure the total amount of the quaternary amines adsorbed in the interphase as a function of its bulk concentration and as a function of the zinc electrode potential. There are several experimental techniques that are possibly useful for such measurements.

Two possible electrochemical methods of adsorption study are differential capacitance measurements and oxidation of the adsorbed inhibitor. The difficulty with the latter technique is that it necessitates an assignment of a fraction of a total current to the oxidative process of the adsorbate; such assignment in the case of a zinc electrode which has a large exchange current density is tenuous at best. The situation with any differential capacitance technique is even more arbitrary in that a model must be invoked in order to arrive at an amount adsorbed. The overriding difficulty of both methods, however, is that hydrogen is adsorbed in the potential region of interest.

The situation with non-electrochemical techniques is marginally better. The obvious methods here are of two kinds: analytical determination of the change in bulk concentration of adsorbate and measurement of the amount of adsorbate on (or very near) the electrode. The difficulty inherent in the first method is the very low (ca. 10^{-5} M) bulk concentration of the adsorbate; few techniques are available for determining quaternary amines at this concentration level. Two techniques are available for measurement of the total amount adsorbed. They are ellipsometry and radiotracers.

PRELIMINARY INVESTIGATIONS

Preliminary investigations with the ellipsometric method showed it to be unsuitable for the present problem. The essential difficulty was the impossibility of maintaining a specularly reflective zinc electrode surface. The experimental conditions were such that roughening of the zinc surface was unavoidable.

The above considerations effectively limit the suitable methods of study to radioactive techniques of which there are two general types. Those in which count rates are determined in situ and those in which the adsorbent is removed from the bulk adsorbate and counted externally. The latter type of technique was chosen as the type most amenable to the present problem.

The technique selected was developed in this laboratory in the early 1960's by Swinkels, et al². In essence, the method consists of adsorbing C¹⁴ labeled organic compounds on a continuous metal tape, which is connected as a working electrode in a usual 3-electrode potentiostat circuit. The tape electrode, when slowly withdrawn from the cell at a uniform speed through a slit, has only a quite thin (ca. 1 micron) film of solution on it. The amount of C¹⁴-labeled compound adsorbed on the tape (together with that in the adhering solution film for which a correction can be made) is determined by means of two parallel - one above and one below the tape - gas flow proportional counters.

EXPERIMENTAL DIFFICULTIES

The two experimental difficulties immediately encountered were insufficient sensitivity of the radiation detection system and grossly irreproducible solution film thicknesses. Radiation detection system sensitivity is improvable to a large extent by changing the detectors and/or their geometry. The more serious problem is that of film uniformity.

The obvious cause of the latter difficulty was, of course, the slit system. The slits were first fabricated of Teflon. The Teflon has both a low hardness and a low surface free energy. The low hardness and lack of dimensional stability of the Teflon is the cause of excessive wear when used in conjunction with the metal tape electrode. More serious still is the low surface free energy of the Teflon, the result of which is that it is not water wet whereas the tape electrode is; the mechanical instability thus created causes the film thickness to be unduly sensitive to slight pressure changes at the exit slit.

EXPERIMENTAL DETAILS

A new cell with glass exit slits was designed and built (see previous reports). Even with the most carefully made slits, however, it was not possible to prevent leakage of the solution at the slit, tape, solution juncture when even very low gas pressures were applied to the drying compartment. It is, of course, necessary to do this in order to sparge the solution. The ultimate solution to this problem was the careful and accurate regulation of a vacuum system (water aspirator as a source) connected to both the cleaning and adsorption cells. The sparging gas, He, was admitted through the drying compartment. Very fine metering valves (Nupro) were found suitable for control of the pressure and vacuum systems.

The insensitivity of the radiation detection system was traced to the anode in the gas flow detectors. New anodes were fabricated in the laboratory from 1 mil platinum wire which was soldered

onto a stainless steel tube that was made part of an HN connector. With the new anodes and using PR-10 gas, the detectors exhibited Geiger regions of over 300 volts with a slope of about 2% per 100 volts.

Since the E_{max} for the beta decay of carbon 14 is about 150 keV, the thinnest possible windows are required for the detectors in order to gain sensitivity sufficient to make meaningful measurements on the very small amounts of radiation to be measured (of the order of 10^{-9} moles). Micro ($85 \mu\text{g}/\text{cm}^2$) gold foil windows are the best available choice of windows in as much as they are the least adsorptive ones obtainable.

The tape detector system was calibrated with labeled $\text{Na}_2\text{C}^{14}\text{O}_3$. A 0.001 M solution of the $\text{Na}_2\text{C}^*\text{O}_3$ was prepared by determinative weighing. A small quantity (typically 0.1 ml) of this solution was placed on a clean tape with a micropipette and allowed to spread. The tape was located between the detectors in the same position it would occupy when adsorption were made. The apparent counter efficiency obtained was 190%. Note that this figure represents the total number of counts by two detectors divided by the calculated number of disintegrations per cm^2 of tape. The actual area of tape counted is indeterminate, but in excess of 10 cm^2 .

In the actual adsorption studies the procedure was to clean the tape in the cleaning cell which contained 1 M NaOH in conductivity water by alternate oxidation then reduction of the electrode. The bright electrode was then moved through the drying compartment which contained dry He to the adsorption cell. In the adsorption cell the Zn tape electrode was potentiostated at a pre-selected potential using a saturated calomel electrode as reference. The tape potential was

maintained for a time sufficient to allow the establishment of adsorption equilibrium. The amount of time required - on the order of 15 minutes - was determined experimentally by plotting observed count rate vs time of adsorption. After the suitable period of time had elapsed, the tape, still under potential control, was moved from the adsorption cell to its position between the two gas flow detectors and counted. The count time was adjusted so that at least a minimum of 1,000 counts was recorded.

EXPERIMENTAL MEASUREMENTS CARRIED OUT

Adsorption measurements were made on zinc tape of 99.999% purity which was furnished by Cominco American, Spokane, Washington, in the form of a strip 2 mils thick by 500 mils wide. The adsorption solution was prepared by diluting a stock solution of the appropriate quaternary amine with 1 M KOH to give the desired concentrations. The concentrations selected for study were: 10^{-6} M, 2.5×10^{-6} M, 5×10^{-6} M, 7.5×10^{-6} M, 10^{-5} M, and 2.5×10^{-5} M. The cetyl trimethyl ammonium bromide used was furnished by Amersham/Searle with a specific activity of 6 mCi/mM.

RESULTS

Results of these experiments indicate that cetyl trimethyl ammonium bromide is strongly adsorbed at potentials within 200 mv of the open circuit potential (ca. -1.5 V vs SCE). The amount adsorbed in this potential region is only weakly concentration dependent. At potentials more than 200 mv cathodic to the open circuit potentials the quaternary amine desorbs strongly.

The at first surprising result that an organic cation is desorbed by a negatively charged electrode is at second glance quite reasonable. At the large potential drops in the electrical double layer during the extreme cathodic polarization to which the stated condition corresponds, it would be expected that small inorganic cations (in this case K^+) and even water dipoles could displace the large quaternary amine cations.

Less conclusive experiments with tetraethyl ammonium bromide indicate somewhat similar behaviour but with desorption occurring at less cathodic potentials than with the cetyl ammonium bromide. This result would argue for the case of the cetyl quaternary amine in preference to a smaller one for dendrite inhibition.

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CONCLUSIONS

- (1) NR_4^+ ions are suitable for dendritic growth inhibition because of the highly -ve position of the potential of zero charge.
- (2) In the absence of satisfactory results for the concentration dependence, we do not know if the adsorption effects are heterogeneous.

FURTHER WORK NEEDED

The ideal dendritic inhibitor would be one in which there is a minimal concentration in solution for blockage of the rotation of spirals which is the preliminary to dendritic growth.

We need, therefore, a study of adsorption heterogeneity to determine where the ions are going, and we need examination of a series of cations to get the law between inhibition and size.

WORK OF MR. R.K. SEN

THEORETICAL CONTRIBUTIONS TO ELECTRODE PROCESSES

GENERAL DESCRIPTION OF WORK.

Mr. Sen was put to work on a variety of theoretical problems which came up in discussions during 1970 and 1971 of batteries and their problems. In the following, the work is reported.

A summary is then given of the findings.

VARIATION OF THE COEFFICIENT OF FRICTION WITH
POTENTIAL FOR A SOLID-SOLUTION CONTACT:
A REVISED CALCULATION

~~CONFIDENTIAL~~

VARIATION OF THE COEFFICIENT OF FRICTION WITH
POTENTIAL FOR A SOLID-SOLUTION CONTACT:
A REVISED CALCULATION.

Several authors^{1,2} have pointed out that a linear relationship exists between the coefficient of friction for a wet contact and the associated potential difference. Bockris, Argade and Gileadi³ reported experiments showing a parabolic relation between friction and the potential difference. Bockris and Argade⁴ then attempted a quantitative calculation of the dependence. The essential aspect of their model was as follows:

The coefficient of static friction is given as:

$$\mu_f = F/R,$$

where F is the frictional force, i.e., the tangential force required to separate the region of microcontact. Then $F = \alpha_T A_0$, where α is the tensile strength of the softer of the two metals in contact and A_0 is the area of microcontact. R is the normal reaction, given as:

$$R = [w \cos\theta - F_a(A - A_0)] - \rho_0 A_0 + F_{el}(A - A_0),$$

where w is the weight of the slider, θ is defined in Fig. 1, F_a is the attractive force per unit area between the solids not in contact, ρ_0 is the attractive surface field force per unit area in the microcontact region and F_{el} is the net repulsion between the double layers per unit area.

However, it can be shown that if Amontons law is valid⁵, i.e., the coefficient of friction is independent of the geometric area of the contact and the weight of the slider, then

$$w \cos\theta + F_{el}(A - A_0) \gg \rho_0 A_0 + F_a(A - A_0).$$

So eq. (1) then becomes

$$\mu_f = \frac{\sigma_T A_0}{w \cos\theta + F_{el}(A - A_0)} \quad (3)$$

To estimate F_{el} Bockris and Argade's⁴ analysis involved the calculation of the repulsion of two plane sheets of charge, i.e., the other side of the charge on each double layer. This probably is an unacceptable simplification. In the present note, the problem is resolved on the following model: it is assumed that in the double layer concerned, specific adsorption is relatively small. In that case, it is possible to regard the interaction approximately as that between two Gouy layers*. This repulsion can be calculated by getting the double layer field due to one double layer at x and finding out the force it exerts on the diffuse layer charges of the other double layer, taking q_{diff} to be localized as a sheet of charge at $1/\kappa$ distance from the solid surface - see fig. 2a. Hence,

$$F_{el} = q_{diff}(-\kappa\psi_0 e^{-\kappa x}) + q_M(-\kappa\psi_0 e^{-\kappa(x + 1/\kappa)}). \quad (4)$$

Under the assumptions made above $q_M = q_{diff}$. Hence,

$$F_{el} = q_{diff}\kappa\psi_0 [e^{-\kappa x} - e^{-\kappa(x + 1/\kappa)}]. \quad (5)$$

Substituting

$$q_{diff} = \frac{(\epsilon n^0 kT)^{1/2}}{(2\bar{\Lambda})^{1/2}} \psi_0 \frac{Ze_0}{kT}$$

in eqn. (5) yields

* Repulsion of two Gouy layers was also calculated by Frumkin⁶ using a different approach.

$$F_{el} = \kappa \left(\frac{\epsilon n^0 kT}{2\bar{\Lambda}} \right)^{\frac{1}{2}} \frac{Ze_0}{kT} \psi_0^2 \left[\exp\{-\kappa x\} - \exp\left\{-\kappa \left(x + \frac{1}{\kappa}\right)\right\} \right]. \quad (6)$$

On the other hand, expressing $\kappa\psi_0$, eq. (5), in terms of q_{diff} yields

$$F_{el} = \frac{4\bar{\Lambda}q_{diff}}{\epsilon} \left[\exp\{-\kappa x\} - \exp\left\{-\kappa \left(x + \frac{1}{\kappa}\right)\right\} \right]. \quad (7)$$

Introducing eq. (6) or (7) in eq. (3) yields eqs. (8) and (9)

$$\mu_f = \frac{\sigma_T A_0}{w \cos\theta + \kappa \left(\frac{\epsilon n^0 kT}{2\bar{\Lambda}} \right)^{\frac{1}{2}} \frac{Ze_0}{kT} \psi_0^2 [e^{-\kappa x} - e^{-\kappa(x + 1/\kappa)}] (A - A_0)}, \quad (8)$$

and

$$\mu_f = \frac{\sigma_T A_0}{w \cos\theta + (4\bar{\Lambda}q_{diff}^2/t) [e^{-\kappa x} - e^{-\kappa(x + 1/\kappa)}] (A - A_0)}. \quad (9)$$

The weight of the slider was 7.1 g, $\alpha_T = 1.266 \times 10^6 \text{ g cm}^{-2}$; A_0 was evaluated by Argade⁷ and was found to be 7.2×10^{-6} . Eq. (9) was evaluated for $x = 6 \times 10^{-7} \text{ cm}$ and $\kappa = \frac{1}{3} \times 10^7 \text{ cm}^{-1}$; q_{diff}^2 was obtained from the integration of the C-V plots. The results are shown in fig. 3 and compared with experiment. The agreement seems fair.

Argade's experiments further showed that when the ring was made of quartz a similar dependence of μ_f on potential was obtained. The explanation of this phenomena can also be obtained from the above theory. The quartz being an insulator can be approximated to a very lowly conducting semiconductor having a very large Debye length ($1/\kappa_1$). This can very easily be shown, e.g., for an intrinsic semiconductor

$$n_{in} = (N_C N_V)^{\frac{1}{2}} (\exp[-E_g/2kT]),$$

and

$$\kappa_1 = [8\bar{n}_{in} e^2 / \epsilon kT]^{1/2}.$$

Taking $\epsilon = 4$ and E_g , the band gap, of 0.7 eV, κ_1 comes out to be $5.85 \times 10^4 \text{ cm}^{-1}$, i.e., $1/\kappa = 1.7 \times 10^{-4}$.

Now the model is as shown in fig. 4 and following essentially the same principles used above, we can write

$$F_{e1} = \left(\frac{\epsilon n_o kT}{\Lambda} \right)^{1/2} \frac{Ze_o}{kT} \psi_o^2 [e^{-\kappa x} - e^{-\kappa(x + 1/\kappa_1)}].$$

Now F_{e1} can be evaluated for $1/\kappa = 3 \times 10^{-7} \text{ cm}$, $1/\kappa_1 = 1.7 \times 10^{-4} \text{ cm}$ and $x = 6 \times 10^{-7} \text{ cm}$. The value of F_{e1} was used to calculate μ_f from eq.

(3). The values are plotted in curve 2 of fig. 5. The agreement again is fair.

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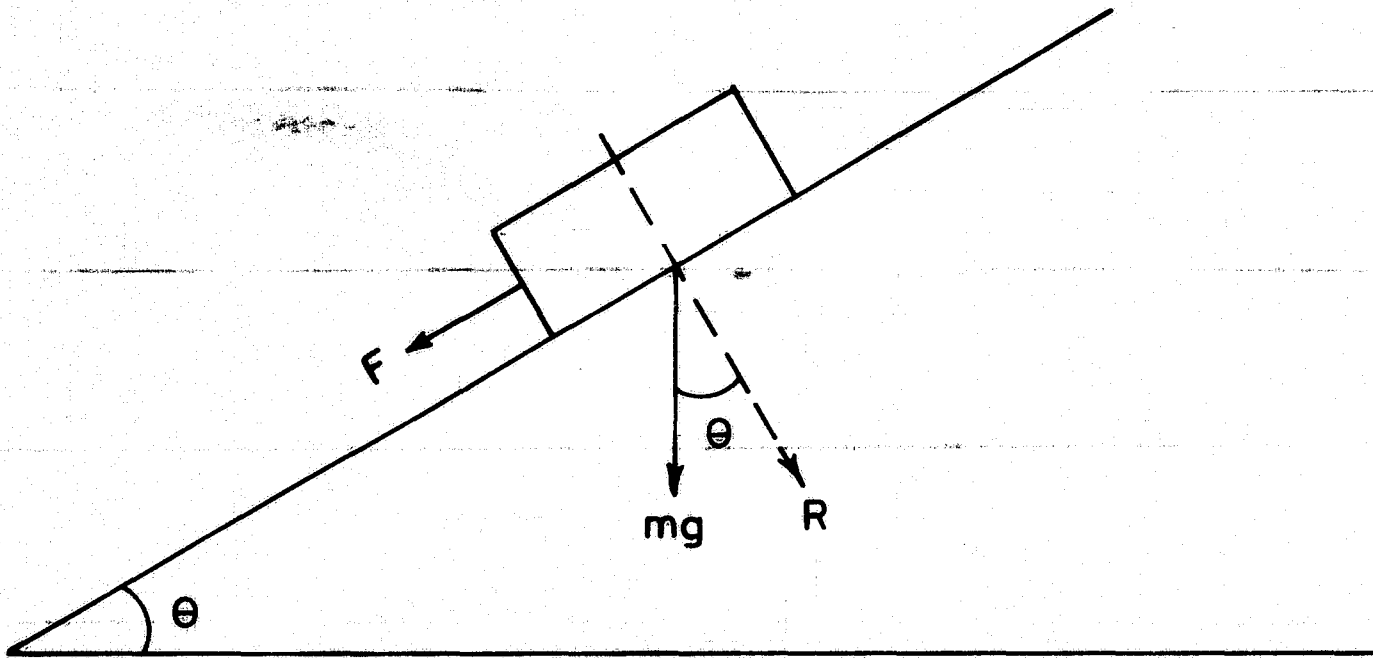


Figure 1.

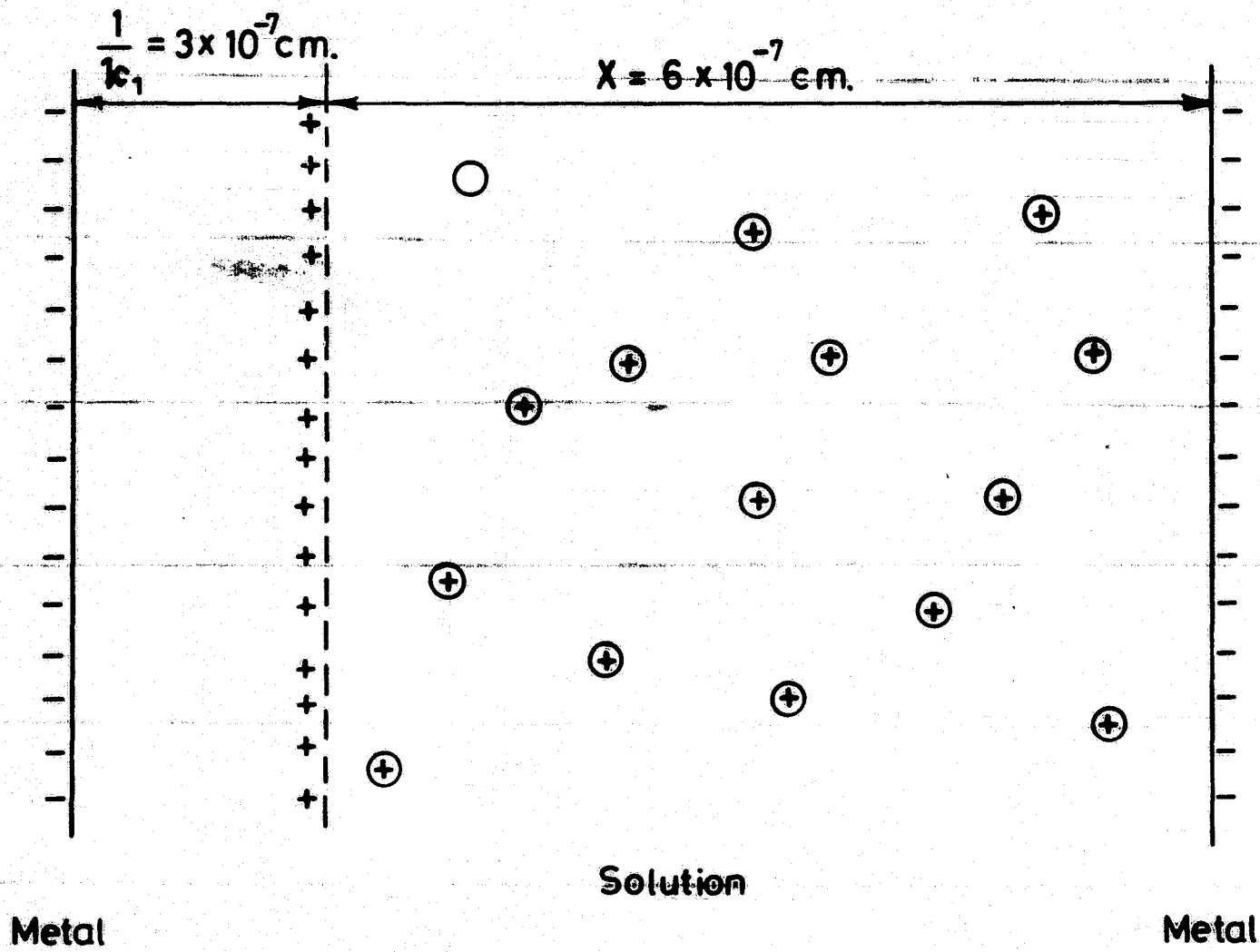


Figure 2

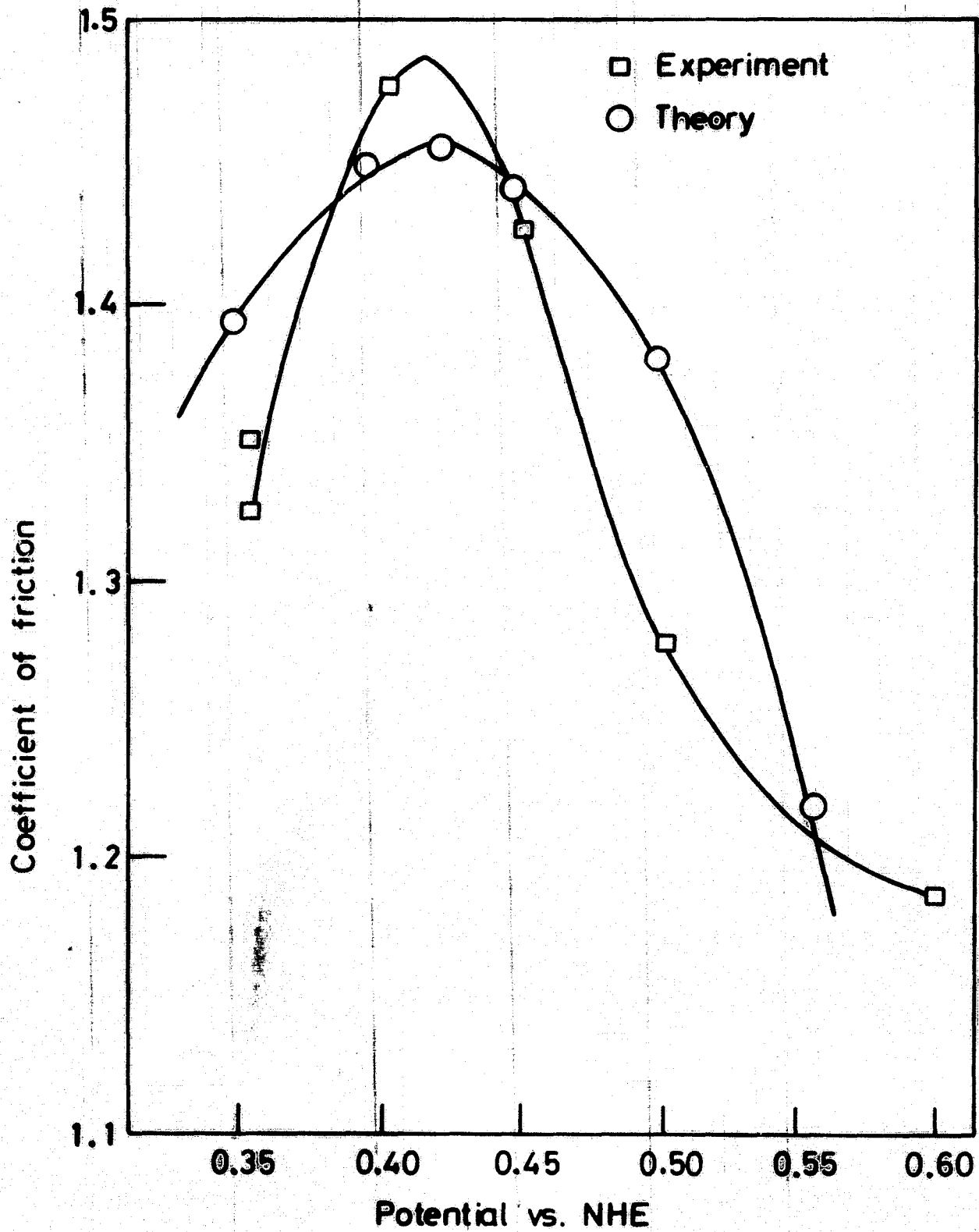


Figure 3.

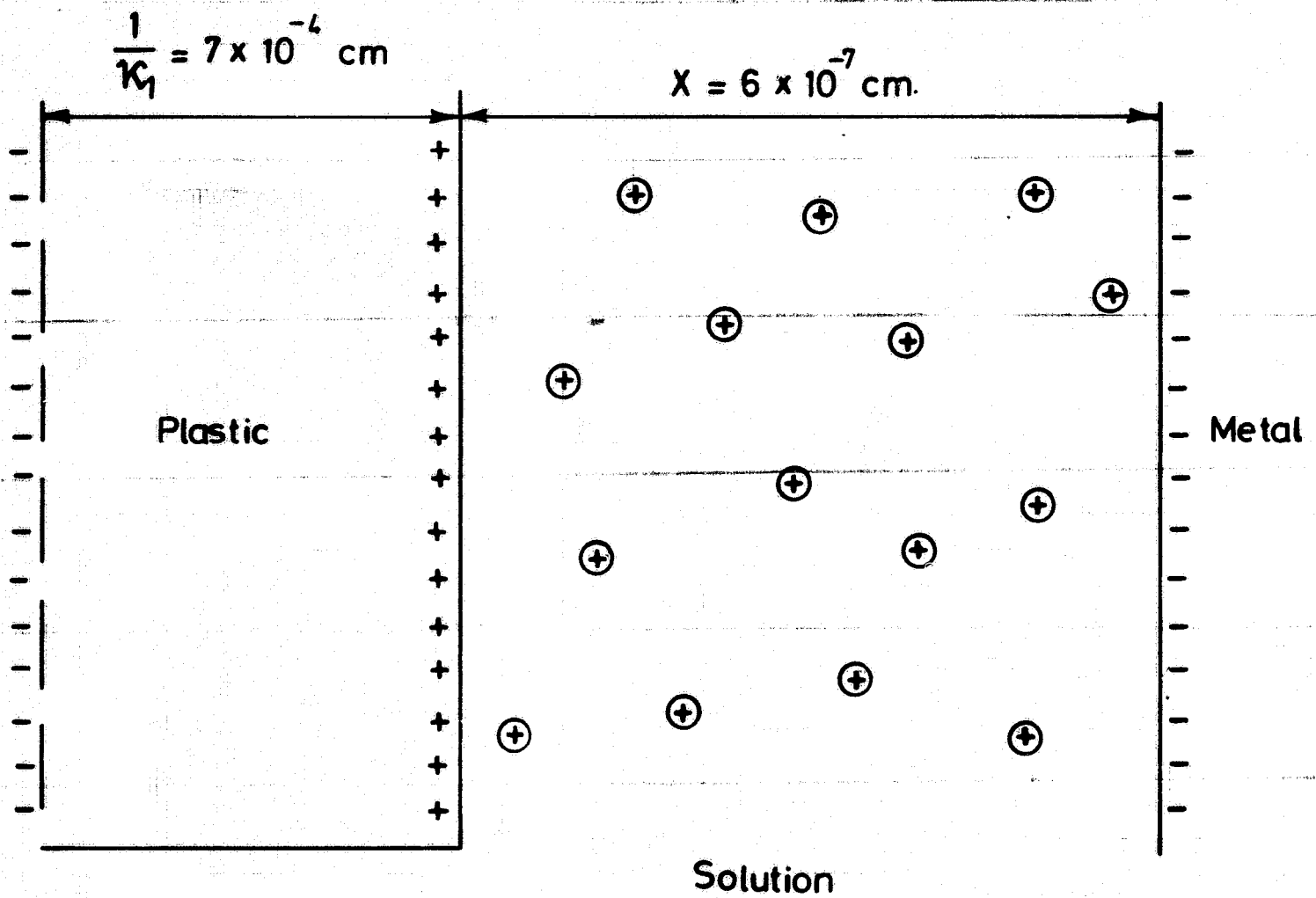


Figure 4.

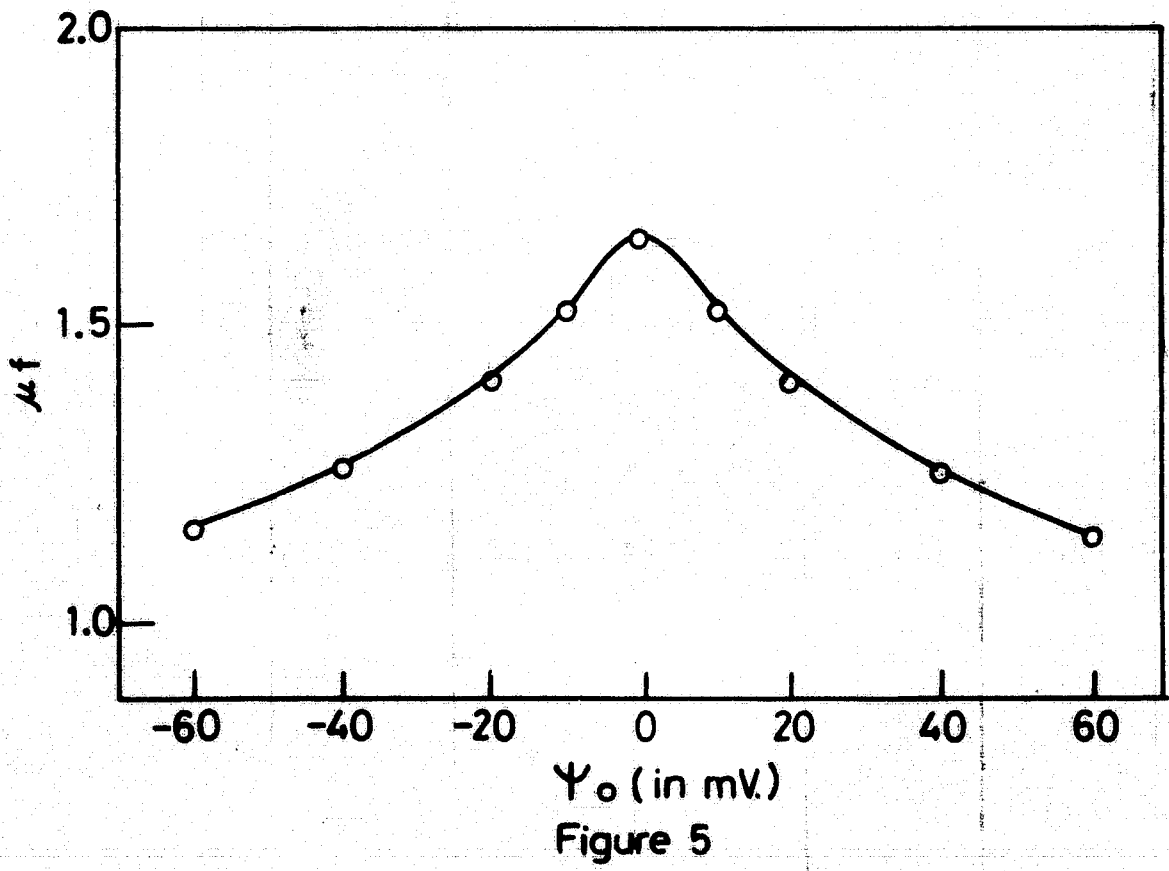
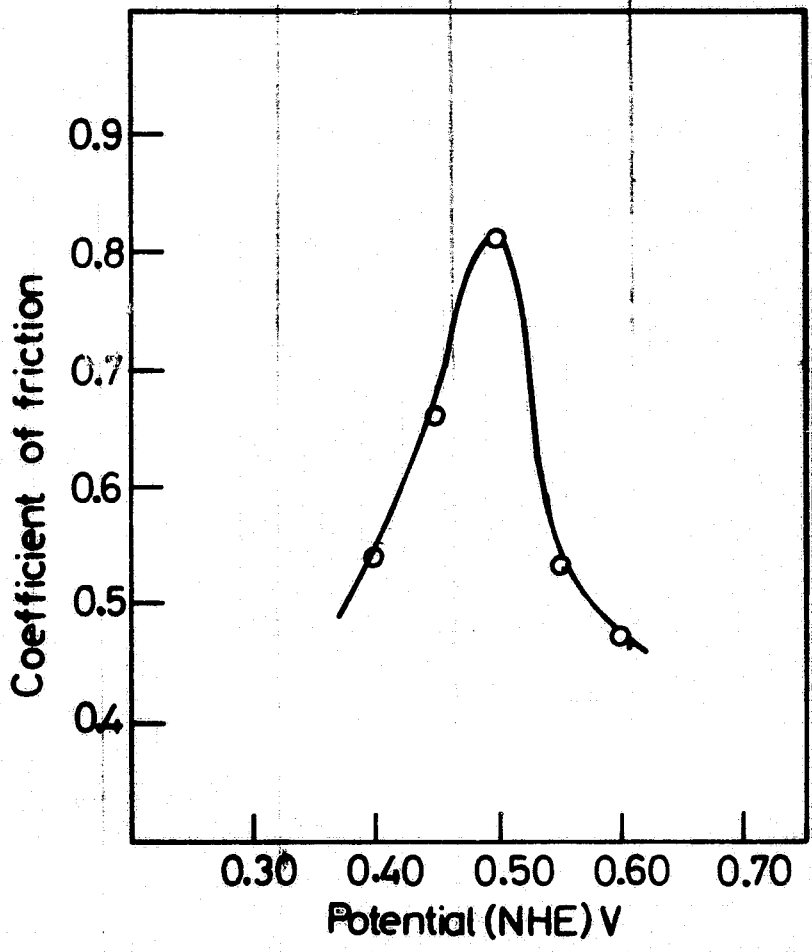


Figure 5

ANNOTATIONS TO FIGURES

Figure 1. Forces involved in friction.

Figure 2. Model of interactions of the Gouy layers between two metal plates.

Figure 3. Coefficient of friction versus potential for Pt on Pt in HClO_4 .

Figure 4. Model of two interacting Gouy layers between a metal and a semiconductor.

Figure 5. Variation of the coefficient of friction with potential at metal-quartz junction. (a) Experiment; (b) theory.

DEVELOPMENTS OF THE BDM MODEL OF THE DOUBLE LAYER

DEVELOPMENTS OF THE BDM MODEL OF THE DOUBLE LAYER

Abstract

Following the publication of the Bockris-Devanathan-Muller model of the double layer, several discussions in support and against various aspects of that model have appeared. A critical discussion of the present status of the model is presented.

I. INTRODUCTION

In 1963 Bockris, Devanathan and Muller¹ (BDM) published an attempt modelistically to interpret several facts, at that time unrationalised, concerning the double layer at a mercury-solution interface, namely: (1) The capacity is constant at $16\mu\text{F cm}^{-2}$ for the double layer region on Hg, whilst the cation size is varied. (2) There is an inflection in the experimental $q_{\text{anion}} - q_{\text{metal}}$ relation. (3) There is a hump on the capacity-potential curves. (4) The relation between coverage on the surface of Hg with organic molecules and the charge of the electrode is parabolic and symmetrical, if small aliphatic molecules are being adsorbed.

BDM explained the independence of the double layer capacitance upon cation size by modifying a proposal made by Watts-Tobin, Mott and Parsons², where it was suggested that the capacitance could be explained in terms of that of a low dielectric water layer; and a high dielectric second layer, further out towards the solution, in series with the low dielectric layer. The shape of the isotherm and the capacitance hump were explained in terms of anion repulsion among the specifically adsorbed molecules. A calculation of the charge at which the capacitance hump occurs has been shown to agree well with the available data⁷. The parabolic

dependence of coverage on potential for the adsorption of aliphatic organic molecules was interpreted in terms of the dependence of the strengths of attachment of the water dipoles to the electrode, the dipoles having a two state configuration. It is the turning round of the water molecules which causes the maximum in adsorption of an organic. The presence of quadratic terms in the field, arising from the polarisability term, was shown to be numerically insufficient to explain the observed parabolic θ -V shape. Bockris, Gileadi and Muller³ (BDM) published a better approximation of the BDM model for organic adsorption, in which both solvent solute dipoles interact with the field. Coverage-charge relations of numerous shapes were deduced. However, the lateral interactions between adsorbed organic particles and between organic and water molecules, were still neglected.

Thus, the BDM model features potential-dependent water molecules as a primary constituent of the double layer; differs from a previous model² in holding the distance of closest approach of non-specifically-adsorbed ions as outside this water layer; and attributes the capacitance hump to anion repulsion rather than to a contribution to the capacitance due to water molecules⁶.*

Support for the BDM model in terms of the isotherm⁷ was also given by Wroblowa and Muller⁸, who showed that the model's neglect of imaging in

* A water capacitance hump is also implicit in the BDM model. Whether one observes a capacitance hump due to anion repulsion, or to water orientations⁶, turns out¹ to depend on the water-water interaction energy, which has been neglected in the approximations of Mott and Watts-Tobin⁶ and of MacDonald and Barlow^{2,3}. In BDM's evaluation, these interactions are shown to make water give a capacitance too large to be observed. Anion humps are qualitatively consistent with the qualitative facts of hump-dependence of anions. Whether capacitance humps are always anionic will depend on solvent as well as anion.

the solution gave a better agreement with experiment than the consequences of the assumption that there is perfect electrostatic imaging at both the metal surface and the OHP (which involves the assumption that there is a sharp electrostatic discontinuity between the double layer and solution regions). Gileadi⁹ has shown that the terms (of water-electrode interaction) used in the BDM model for organic adsorption, have a much greater numerical weight (in the potential range accessible experimentally), than terms representing the change of energy of the double layer which arises in the classical thermodynamic approach¹⁸ to the coverage-charge relation of organic adsorption (cf. the earlier discussion by Wroblowa and Green¹⁷). Gileadi and Stoner¹⁰ have developed the BDM model, with respect to the dipole contributions to the double layer potential, as an interpretation of anomalous current potential relations. Reddy¹¹ has reaffirmed the model, with special reference to the water contributions. Barradas¹² has argued that BGM³ model represents consistently some phenomenology of organic adsorption. Bonciocat¹³ has shown that the BDM isotherm gives rise not only to the hump, but also to the minimum in capacitance observed at potentials positive to the hump, and that the isotherm rationalizes the temperature dependence of the hump. Isotherms which take into account multiple imaging, such as that of Levine, Bell and Calvert, or MacDonald and Barlow, do not do this. Levine, Mingus and Bell¹⁴, and MacDonald and Barlow¹⁵, had criticised the BDM model because of its lack of multiple imaging (cf. Wroblowa and Muller⁸). An alternative theory⁶, in terms of capacitance humps in terms of water rotation capacitance, competes with the BDM model. Damaskin¹⁶ has suggested that consequences of the BDM model of organic adsorption are inconsistent with thermodynamic reasoning. He has suggested

that a neglect of the energy of charging the double layer is important (but cf. Gileadi⁹, Wroblowa and Green¹⁷). The neglect of electrode-organic interactions in the original BDM has been criticised by Frumkin¹⁸, but this objection is no longer relevant because a second approximation of BDM (that of GBM) took this into account. The neglect of a polarizability term in $\frac{1}{2}\omega F^2$ has been criticised also by Damaskin¹⁶. Mohilner¹⁹ has suggested that the dipole potential arising from the BDM model is too large.

II. DEGREE OF CONSISTENCE OF THE BDM MODEL

1. The Ionic Adsorption Isotherm

The BDM isotherm can be represented in the form:

$$\ln \frac{\theta}{1-\theta} = -\Delta G^0/RT + \ln \frac{a_{\pm}}{a_0} + Aq_M + B\theta^{3/2}. \quad (1)$$

This isotherm is obtained using single imaging for the evaluation of the lateral interaction terms. Levine, Bell and Mingu¹⁴ and MacDonald and Barlow¹⁵ preferred multiple imaging. The multiple imaging results in a higher screening effect, decreasing the lateral interaction energy, which then becomes proportional to θ instead of $\theta^{3/2}$ obtained by BDM. Thus, the Levine, Bell and Calvert²⁰ isotherm is of the form:

$$\ln \frac{\theta}{(1-p\theta)^p} = -\frac{\Delta G^0}{RT} + \ln \frac{a_{\pm}}{a_0} + Aq_M - C\theta, \quad (2)$$

where $p = r_{\text{anion}}/r_{\text{water}}$ (assumed approx. 1 in BDM).

Which of the two approximations for imaging agrees more closely with the physical situation? The tests that can be carried out are (1) plotting the $\log a_{\pm}(1-\theta)/\theta q_M$ vs $\theta^{3/2}$ and $\log a_{\pm}(1-p\theta)^p/\theta q_M$ vs θ , to examine the linearity as well as the slope from experimental data, and (2) by examining the Essin-Markhov effect. Wroblowa and Muller⁸ made these tests

and their results can be summarised as (1) the slopes B and C of equation (1) and (2) when compared with experiment from the above mentioned plots, show that the predictions of B from BDM model agree within about 15-20% of the experimental results, whereas the C values predicted by the LBC isotherm, taking $p = 1$, exceed the experimental ones by four to twelve times for the anions Cl^- , CN^- , ClO_4^- , ClO_3^- , BrO_3^- and CNS^- , and (2) for $p \neq 1$ the constancy of $\left(\frac{dq_{\text{CA}}^-}{dq_{\text{M}}} \right)_{a_+}$ at coverages usually encountered in ionic adsorption is not obtained from the LBC isotherm, whereas the same quantity from the BDM model does almost stay constant.

The single-imaging approximation gains in these tests. Single and infinite imaging are limiting cases of a more complicated situation which neither equation (1) nor equation (2) represents accurately. It is more difficult to think, however, that conductive imaging (the assumption of LBC) in the relatively poor conductor, an ionic solution, will occur to a significant extent. MacDonald and Barlow¹⁵ pointed out that, even in the metal, imaging at molecular distances is not perfect. Due to the lack of sharpness of the dielectric boundary between the OHP and the rest of the solution, dielectric imaging beyond the OHP will be far from perfect, and that is probably why single-imaging gives better agreement with experiment. An estimate of partial imaging, on the solution side, is desirable. Some attempt has been made in this direction by Buff and Goel²⁹. In concurrence with the present discussions, their results show that the more gradual is the change in the dielectric constant the less pronounced is the degree of imaging in the solution.

Recently, Levine³⁰ has recalculated the results obtained by Wroblowa and Muller⁸ from his multiple imaging model, but using a value of $p = 2$, for his isotherm. The term p represents the radius ratio of an ion to water and it is nearer to 1 than 2 for most anions concerned. The use of p as an adjustable parameter and its substitution in LBC decreases the discrepancies with experiment which this model has for $p = 1$, so far as the slope and the Essin-Markhov effect goes. (It is clear that all isotherms should be formulated with a p value of $r_1^2/r_{H_2O}^2$). We, therefore, compare the single and multiple imaging models in respect to the capacitance hump phenomena. In respect to the BDM model, the q_{CA}^- vs q_M curve (and thus the hump, with anion dependence) is predicted⁷, and recently it has been shown¹³ that both the capacitance hump and the subsequent minimum are predicted by the BDM theory. Let us see whether the prediction of humps from an LBC isotherm is also consistent with experiment. The LBC isotherm can be written ($p = 2$) as:

$$A'q_M = \ln\theta - \ln(1-2\theta)^2 - \ln a_{\pm} - C\theta + \text{constant.} \quad (3)$$

Hence:

$$\begin{aligned} A' \frac{dq_M}{d\theta} &= \frac{1}{\theta} + \frac{4(1-2\theta)}{(1-2\theta)^2} - C \\ &= \left(\frac{1}{\theta} + \frac{4}{1-2\theta} - C \right). \end{aligned} \quad (4)$$

So:

$$\frac{d\theta}{dq_M} = \frac{A'}{\left(\frac{1}{\theta} + \frac{4}{1-2\theta} - C \right)}. \quad (5)$$

$$\text{Let } x = \frac{1}{\theta} + \frac{4}{1-2\theta} - C.$$

Then:

$$\frac{d\theta}{dq_M} = \frac{A'}{x}.$$

Now:
$$\frac{d^2 \theta}{dq_M^2} = \frac{1}{2} \cdot \frac{d}{d\theta} \left(\frac{d\theta}{dq_M} \right)^2$$

$$= \frac{(A')^2}{x^3} \cdot \frac{dx}{d\theta} . \quad (6)$$

Let us now evaluate $\frac{dx}{d\theta}$.

So:
$$\frac{dx}{d\theta} = \frac{d}{d\theta} \left(\frac{1}{\theta} + \frac{4}{(1-2\theta)} - C \right)$$

$$= \frac{1}{\theta^2} + \frac{8}{(1-2\theta)} = \frac{4\theta^2 + 4\theta - 1}{\theta^2(1-2\theta)^2} .$$

Thus:

$$\frac{d^2 \theta}{dq_M^2} = \frac{(A')^2}{3} \left(\frac{4\theta^2 + 4\theta - 1}{\theta^2(1-2\theta)^2} \right) . \quad (7)$$

For the inflection point $\frac{d^2 \theta}{dq_M^2} = 0$.

Thus:

$$\frac{(A')^2}{x^3} \left(\frac{4\theta^2 - 4\theta - 1}{\theta^2(1-2\theta)^2} \right) = 0 . \quad (8)$$

$A' \neq 0$. Thus: $4\theta^2 + 4\theta - 1 = 0$.

Or: $\theta_1 = \frac{1}{2}(\sqrt{2} - 1)$ or $\theta_2 = -\frac{1}{2}(\sqrt{2} + 1)$. (9)

A negative value of θ has no physical significance. Thus, the inflection point is given by the root θ_1 . Hence (cf. relation (9)), the inflection in LBC is independent of any property of the ion, or the value of q_M . Thus, for ions to which the LBC isotherm is intended, the plot of q_{CA}^- vs q_M the inflection should occur at the same point for every anion. This is not

the case. The plot of $q_{\text{inflection}}$ vs q_{hump} would not give a straight line with a slope of unity as is obtained from the BDM theory.

Thus, the multiple imaging approach of Levine et al²⁹ does give less consistence with experiment (qualitatively as well as quantitatively) in its application to predict the inflection on the plot of q_{CA}^- vs q_{M} .

2. The capacitance hump

The most discussed aspect of the recent double layer theory has been the rationalization of the hump observed in capacity-potential relation. The BDM model formulates in terms of single imaging an idea suggested qualitatively by Devanathan²⁰ and supported by Watanabe²¹. In BDM, it is the contribution of the repulsive forces to the standard free energy of adsorption which provides an inflection on the $q_{\text{CA}}^- - q_{\text{M}}$ curve, and thus gives a hump in the $C - q_{\text{M}}$ curves. The BDM ionic adsorption isotherm for low coverage can be written as:

$$\ln \left(\frac{\theta}{1-\theta} \right) = \text{constant} + \ln a_i + Aq_{\text{M}} - B\theta^{3/2}, \quad (10)$$

where constant =

$$\left(- \frac{\Delta G^\circ}{RT} - ma_o \right).$$

The condition for the inflection point in the $\theta = f(q_{\text{M}})$ curve can be written as:

$$2 - 4\theta - \frac{3}{2}B\theta^{3/2} + B\theta^{5/2} = 0, \quad (11)$$

where:

$$B = \frac{\pi^{7/2} e_o^2 r_i^2 \left(\frac{q_{\text{max}}^- N_A}{F} \right)^{3/2}}{4\epsilon kT},$$

where the terms have their usual meaning.

This equation has two roots¹³:

$$\theta_1 = (4/3B)^{2/3} \text{ and } \theta_2 = 1/2 .$$

θ_1 corresponds to a local maximum, i.e., the hump in the $C - q_M$ curve, and θ_2 is the local minimum.

On the other hand, considering the root of the LBC isotherm, it can be shown¹³ that it does represent the maximum. But, since the root θ_1 of the LBC isotherm does not depend on the nature of the anion, the capacitance hump in this approach is independent of the nature of the anions which is at variance with experimental observations²¹. The LBC isotherm furthermore does not predict any minimum after the hump, whereas the BDM model does.

Others^{22,23} consider the hump is due to a solvent effect. There are qualitative objections to the solvent reorientation model for the hump. (i) For common anions except F^- , the region of charge near to the hump sees the onset of anion adsorption²⁴; (ii) the magnitude and location of the hump varies with the anion²⁵; (iii) in some polar non-aqueous solvents, no hump is observed²⁵; (iv) if solvent reorientation did give rise to a maximum in local permittivity, and hence the hump, it would do so for aqueous solutions on the cathodic side of the pzc ²⁴.

In favour of a solvent reorientation theory of the hump is that humps occur for F^- . There is considerable evidence²⁶ that the F^- is not specifically adsorbed. However, this conclusion relies on the applicability of the Gouy-Chapman diffuse layer theory, the assumption of zero specific adsorption of water, etc. It is possible that F^- merely differs in degree of adsorption from other halide ions. The evidence is strong that specifically adsorbed anions play a role in causing the hump. The BDM model quantitatively predicts the phenomenology.

Payne²⁷ found in N-methyl formamide system two humps, one on the cathodic side and the other on the anodic side of the e.c.m. Both BDM and solvent reorientation theories find difficulty in explaining both humps. However, if solvent-solvent repulsion is relatively small, BDM also predicts a solvent capacitance hump as does the interaction-free, antecedent model of Mott and Watts-Tobin⁶. In two hump systems, one hump may be due to anion-repulsion, the other to dipole orientation.

3. Organic Adsorption

The BDM competition theory of organic adsorption is a development of the water competition model proposed by Butler⁴. It will not be applicable to potential regions in which there is significant chemisorbed hydrogen or oxygen on the surface, nor to situations in which there is dissociation of the organic molecule on adsorption. The original version of the model¹ will only be applicable to systems in which there is no electrical interaction of the double layer with dipole moments of the organic molecules. This assumption applies to a situation in which the organic has its polar groups in the diffuse layer, where the field is negligible compared with that on the water dipole, which is inside the compact layer. In the BGM³ approximation, various orientations of the adsorbed species were considered and then interactions with the electric field explicitly calculated. The model was able to interpret most of the shapes of the θ - q_M curves obtained.

(i) Is the BDM model inconsistent with thermodynamic reasoning?

Let us take a general isotherm, congruent with respect to charge of the form:

$$G(q)c = f(\Gamma) \quad (12)$$

where $f(\Gamma)$ is a function of the surface excess, Γ .

Thermodynamic treatment¹⁶ yields an equation of the form:

$$G(q) = G_0 \exp \left[-A^{-1} \frac{(K_0 - c')}{2K_0 c'} q^2 + \int \Delta\chi dq + qE_N^{\text{org}} \right], \quad (13)$$

where G_0 is the value of G at $q = 0$, $A = RT \Gamma$, K_0 is the capacity of the double layer when the coverage of the organic, i.e., $\theta = 0$ and c' is the capacity when $\theta = 1$, q is the charge, $\Delta\chi$ is the surface potential and E_N^{org} is the potential drop due to the oriented adsorption of the organic dipoles.

Similarly, if we take the BDM organic adsorption isotherm which

is:

$$\frac{\theta}{1-\theta} = \frac{C_{\text{org}}}{C_W} e^{-\Delta G_{\text{org}}^0/RT} e^{n\Delta G_c^0/RT} e^{-(Ec/kT)} \left[(4\pi\mu q/\epsilon) - \frac{REC}{kT} \right], \quad (14)$$

we can rewrite it in the form:

$$G(q) = G_0 \exp \left[-nR(\mu X - REC)/kT \right] \quad (15)$$

where $X = \text{electric field strength} = \frac{4\pi q_M}{\epsilon}$,

and R is given as:

$$R = \tanh \left[(\mu X - REC)/kT \right]$$

where $G(q)$ and G_0 have the meaning of equation (13), n is the number of water molecules displaced during the adsorption of a single organic molecule, μ is the dipole moment of water, X is the electric field acting in water, E is the lateral interaction energy between water molecules, and C is the effective coordination number of the water molecules at the electrode.

Equations (13) and (15) differ importantly.

The terms $\left[A^{-1} \frac{(K_o - c')}{2K_o x'} q^2 \right]$ and $\left[qE_N^{\text{org}} \right]$ are absent in (15). Since equation (13) is derived¹⁶ from a charge-congruent isotherm, it should be thermodynamically consistent solution of the problem. As the BDM isotherm, represented by equation (15), omits two terms of the isotherm of equation (13), it has been argued¹⁶ that the BDM isotherm is inconsistent with thermodynamics.

In the derivation of equation (13), given by Damaskin¹⁶, one involves the equation:

$$E = E_o(1 - \theta) + E\theta \quad (16)$$

where E is the total potential*, E' the potential at $\theta = 1$, and E_o is the potential when $\theta = 0$. This equation is based on the modelistic assumption that, at a given charge q, there is a linear variation between E and θ . This will only be true if the free energy of adsorption is not coverage dependent, which is not generally true. This fact has been pointed out by Delahay³¹. Thus, equation (16) is not purely thermodynamic. It represents a model. Consequently, equation (13) cannot be purely thermodynamic. Thus, both equations (13) and (15) involve modelistic assumptions and, as these differ, their consequences would not be expected to be the same.

* E in the Russian literature is defined as the total potential. It is implicitly assumed that the rest of the potential in a cell remains constant so that change in E reflects the change in the potential at an electrode solution interface.

An argument of a similar nature arises because equation (13) is obtained from equation (12), which is an adsorption isotherm based on a model (essentially, electrode-water and electrode-organic interactions are considered), and equation (15) arises from a different model (essentially, interaction of water molecules with the electrode and each other). The first and third term of equation (12) correspond to a change in the double layer energy due to organic adsorption, and the reorientation energy of the organic dipole, respectively. However, the BDM model involves an initial assumption of a condition such that these energies are smaller than the electrostatic interaction of water (and, in BGM, the organic), with the electrode. It may be right to argue that the neglect of change of energy in the double layer due to change of capacitance on organic adsorption is a poor approximation (see next section). However, it is not rational to claim, as did Damaskin¹⁶, an inconsistency with thermodynamic principles because another model (which has been formulated in a way which involved thermodynamic equations) predicts some other behaviour.

(ii) Neglect of the change of the energy of the double layer upon adsorption of the organic:

It has been argued¹⁶ that this approximation in the BDM theory could lead to important discrepancies with experiment. Recently, Gileadi⁹ evaluated the relative contribution of the term corresponding to the energy change due to water dipole reorientation, and the term due to the energy change of the ionic double layer due to organic adsorption. The results are summarised in Table I.

TABLE I

Relative contributions of the Frumkin term and the Bockris

| | <u>et al term</u> | | | | |
|---|-------------------|----|----|----|----|
| Potential in volts | 0.5 | 1 | 2 | 5 | 10 |
| Term corresponding to energy change in ionic double layer % | 7.6 | 14 | 25 | 45 | 62 |
| Water dipole re-orientation term % | 92.4 | 86 | 75 | 55 | 38 |

Table I shows the relative contributions of the two terms to the total variation of the adsorption equilibrium consistent with potential at different values of E. Although the term corresponding to the change of energy of the double layer is not negligible (as assumed in BDM), its contribution will be relatively small over the potential range accessible experiment (~1 volt). Thus, this objection¹⁶ is not a weighty one.

(iii) Is the Electrode Charge predicted for the Adsorption Maximum BDM (or BGM) inconsistent with experiment?

It has been inferred¹⁶ that, since in the BDM theory the maximum of organic adsorption occurs at the point where $N_{\uparrow} = N_{\downarrow}$ the maximum of organic adsorption should occur only at the pzc. Since experimentally this is not observed, the argument was that the BDM model does not predict the experimental results well. This criticism is due to a misreading of the original papers. In BDM, although it is argued that the maximum of organic adsorption occurs at the point where $N_{\uparrow} = N_{\downarrow}$, it is pointed out that this situation should not arise at the pzc, because of the stronger binding of the water molecules in one orientation than

in the other.* Bockris and Swinkels³², using the BDM model, showed that the maximum of organic adsorption will occur when:

$$\left[(\Delta G_C^{\circ\uparrow}) - (\Delta G_C^{\circ\downarrow}) \right] - \frac{8\pi\mu}{\epsilon} \cdot q_{\max} = 0, \quad (16)$$

where $\Delta G_C^{\circ\uparrow}$ and $\Delta G_C^{\circ\downarrow}$ are the free energies of adsorption of water in up and down position.

This is expected for a model in which there is no electrical interaction of the organic molecule with the electrode. For the more general (BGM) model³, in which such an interaction is accounted for, the adsorption maximum will depend not only on the water-electrode, but also organic-electrode interactions. It will, finally, depend on all interactions (e.g., also organic-organic and water-organic), although others may not have a great effect (see Section V) on the adsorption of aliphatic molecules.

(iv) Is there any relation between the hump on the capacitance vs electrode charge curve and the maximum of organic adsorption?

It has been argued¹⁶ that there is a relation predicted by the BDM model between the potential of the hump of the capacitance curve and the potential of maximum organic adsorption. The BDM model predicts that the peak of organic adsorption occurs at the point where $N_{\uparrow} = N_{\downarrow}$. Since the capacitance hump (if it is attributed to the solvent) would also occur at the point where $N_{\uparrow} = N_{\downarrow}$, the two potentials ought to be the same. Experimental results do not show such a correlation. Hence, the BDM model is inconsistent with experiment.

* The difference may arise, inter alia, from the lack of symmetry and hence water-metal image energy, in the two positions.

However, this argument misrepresents the BDM model: the capacitance hump in this model is not generally due to solvent reorientation, but anion repulsion (Section II, 1). There is absolutely no relation, in the BDM model, between the potential or the electrode charge, at which there is an adsorption maximum, and that at which a capacitance maximum occurs - in agreement with experimental observations.

(v) Is the BDM model neglect of organic-organic and organic-water interactions significant?

The neglect of the organic-electrode interactions (one of many approximations in the BDM model) was revised in BGM. Bockris and Swinkels³² made an estimate of the organic-organic interactions, but they have not yet been introduced into the general equations of improvements in the treatment of the BDM model, largely owing to algebraic difficulties. The BDM model has been criticised for neglect of organic-organic interactions. Let us, therefore, make a crude estimate of the importance of organic-organic interactions in organic adsorption. We will assume for simplicity that there are only two positions of the organic molecule. The interaction of a pair of these, when they are pointing in the same direction, is:

$$E_{12} = \frac{\mu_s^2}{\epsilon r^3} \quad (17)$$

Due to the effect of the value of ϵ , E_{12} for water is about 7 times larger than that of the butanol-butanol interaction. Even for $\theta = 0.5$, where the distance between water molecules and the organic molecules are approximately the same, i.e., r is the same, the organic-organic interaction

energies are one-tenth of the water-water interactions. Only when the coverage by the organic approaches 0.8 does the organic-organic interactions become of the comparable order of magnitude as that of the water-water interactions. Thus, neglect of the organic-organic interactions in studying organic adsorption seems a reasonable compromise with the complexity of the expressions relating coverage to electrode charge. However, organic-organic interactions at higher coverage may dominate the interaction situation where the organic dipole lies on the electrode (see Fig. 1). In such a case, the objection is valid.

In a recent article Dutkewicz, Garnish and Parsons³⁴ showed that for 1:4 butane diol and 1:4 but-2-yne diol the charge dependence of the free-energy of adsorption does not give the same result as obtained from the Bockris, Devanathan and Muller theory. They have interpreted the discrepancy as arising due to the neglect of the water-organic interactions. It is clear that organic-water interactions should be accounted for in principle, and that they will become significant if the dipole of the organic sits in a position where it is exposed to a field of about the same magnitude as that of the water. The BDM formulation would apply when the organic dipole is in the diffuse layer and the approximation gets better in the organic dipole away from the water. The discrepancy would be particularly great if the organic molecules are lying flat on the electrode surface.

However, physically when the organic polar groups are in the high dielectric constant region, whereas the water dipoles are in the low dielectric constant region, there seems to be little reason why the interaction should become very important.

(vi) Neglect of the polarizability term in electrode molecule interaction:

It is trivial to show that, for $(q_M) < 10\mu \text{ coul cm}^{-2}$:

$$\frac{1}{2}(\Delta\alpha)\chi^2 \ll (\Delta\mu)\chi$$

where $\chi = \frac{4nq_M}{\epsilon}$ and ϵ is taken as 6. This conclusion assumes the two-state water dipole model, and in both, the dipole is perpendicular to the electrode.

At $q_M > 10\mu \text{ coul cm}^{-2}$, the polarizability term will become increasingly significant and should be included in a further approximation for the model. However, it is important to note that the small value of $1/2\alpha\chi^2$ (or $\frac{1}{2}CV^2$) compared with $\mu\chi$, at $\chi \rightarrow 0$, means that change in direction of the coverage-charge relation cannot arise (as in the former models), by virtue of the quadratic term. It is therefore necessary to have some change in position of an electrically interacting entity in the double layer, near the adsorption maximum. This was the origin of BDM's suggestion that this change is in the orientation of the water dipole.*

4. Surface Potential:

Mohilner¹⁹ stated that, assuming full coverage of the electrode

* The two state model assumed for water is, of course, also an approximation (cf. MacDonald and Barlow, who discussed a multi-state arrangement). The effect of several molecular orientations in respect to sample organic molecules is formulated in BGM. The symmetry of the θ - q_M relation often observed does support the two-state model for water in BDM. However, other possibilities (which would reduce the dominance of the water effects) are: (a) The introduction of a degree of dimerization; (b) A two state model in which the effective dipole moment is reduced due to orientation other than vertical.

with water molecules, the value of the surface potential $\Delta\chi$ from the BDM model is unrealistically high.

In the BDM theory (and for an organic of zero dipole moment):

$$\Delta\chi = \frac{4\pi\mu N_T}{\epsilon} \tanh\left(\frac{\mu\chi}{kT} - \frac{REc}{kT}\right), \quad (18)$$

where $R = \tanh\left(\frac{\mu\chi}{kT} - \frac{REc}{kT}\right)$.

Moreover, to eliminate the water hump in the capacitance potential curve, $\frac{d\chi_{\text{dipole}}}{dq_M} < 0.01$ when $q_M = 20\mu \text{ coul cm}^{-2}$.

$$\text{i.e., } \frac{\partial\chi_{\text{dip}}}{q_M} = \frac{1}{C_{\text{dip}}} = \frac{8\pi^2\mu^2 N_T}{\epsilon^2 kT} \frac{(1-R)^2}{1 + \frac{Ec}{kT}(1-R^2)} < 0.01. \quad (19)$$

In judging what parameters should be used to test this equation, there are two constraints. The change of $\Delta\chi$ with potential must not be too high, because if it is, it will not be consistent with the observed linearity of the Tafel line.

Now:

$$\Delta\chi = \frac{4\pi\mu_{\text{H}_2\text{O}} N_T}{\epsilon} \tanh\left(\frac{\mu\chi}{kT} - \frac{REc}{kT}\right) < 0.1 \text{ volt}$$

and
$$\frac{\partial\Delta\chi}{q_M} = \frac{1}{C_{\text{dip}}} = \frac{8\pi^2\mu N_T}{\epsilon^2 kT} \left[\frac{1-R^2}{1 + \frac{Ec}{kT}(1-R^2)} \right] \ll 0.01.$$

Evaluating these two equations with the above constraint yields $\Delta\chi \approx 100 \text{ mv}$ for $N_T \approx 10^{14} \text{ molecules/cm}^2$ for $\frac{E}{kT} = 0.5$ (the value assumed by BDM). The problem is that the value of N_T thus required is significantly less than the close packing value for the water molecules. To obtain a total coverage of only $c.10^{14} \text{ molecules/cm}^{-2}$, $r_{\text{H}_2\text{O}} \approx 3.9\text{\AA}$ instead of 1.4\AA .

How may we reduce this difficulty? Examination of the above equation shows that, as we increase the value of $\frac{E}{kT}$, the value of $\frac{1}{C_{\text{dip}}}$, and also the value of $\Delta\chi$, also decreases. For $\frac{E}{kT} \approx 1$, the value of $\Delta\chi \approx 100$ mv is obtained for $N_T \approx 5 \times 10^{14}$ molecules/cm², which is the close packing value if we assume the radius of water to be $\approx 2\text{\AA}$. The problem, therefore, is physically to rationalize the value of $\frac{E}{kT} \approx 1$. Let us assume that the lateral interaction energy is given by dipole-dipole forces plus the quadrupole-quadrupole forces. Thus:

$$E = E_{\mu\mu} + E_{QQ} = \frac{\mu^2}{R^3} + \frac{P^2}{R^5}.$$

Evaluating this for interaction between two water molecules separated by 2\AA , yields $E_{\mu\mu} \approx 0.5$ Kcal/mole and $E_{QQ} = 0.08$ Kcal/mole. So, $E = 0.58$ Kcal/mole. Hence, $\frac{E}{kT} = 0.966$ which is near to the value needed to give reasonable agreement for the close packing value of N_T . Thus, a reasonable value for $\Delta\chi$ does arise on a BDM model if a better approximation is used for E , the water-water interaction energy.

III. PRESENT POSITION OF THE BDM MODEL

The BDM model gives a prediction of humps with those observed: its prediction of linearity in $\log a_{\pm} - \log \frac{\theta}{1-\theta}$ versus $\theta^{\frac{1}{2}}$ is consistent with experiment. Some degree of multiple imaging should be introduced, but it must be less than that of the multiple imaging models to retain the consistencies of the single imaging model. The BDM model is consistent with a solvent hump, if the lateral interaction among the solvent molecules is low enough.

For organic adsorption, some of the criticisms published involved misunderstanding of the model, e.g., that about the position of the hump, the peak of organic adsorption, and that which neglected the BGM organic interactions. The most serious criticism, that the model was in disagreement with thermodynamics, is not correct: BDM is not consistent with another model, which has used thermodynamics in its formulation. The neglect of the ionic double layer energy seems a reasonable approximation over the potential range accessible.

The three principal contributions of the BDM model are the consequences of interactions among water in a two state model; the demonstration that such a model rationalizes the θ - q_M parabolas for aliphatic adsorption (and that models which rely on quadratic terms in V or q will not do this); the position of the outer Helmholtz plane as being outside this layer; and the demonstration of a reasonable degree of consistence with experiment for single imaging. These contributions seem not to be challenged by valid criticism. The most important directions in which the model should be developed is in respect to a better evaluation of the water-water interactions, with an examination of the effects of various other configurations for water, the inclusion of organic-water and organic-organic interactions, and perhaps an attempt at a realistic multiple imaging calculation. The last modification seems the least needed (in respect to consistency of ionic isotherms with experiment) and the most difficult³³.

The continued neglect of contributions to the double layer properties of the potential dependent water dipoles, except by MacDonald and Barlow²³, seems the major anomaly of the last decade of double layer research.

IV. GENEALOGY OF THE BDM MODEL

Lange and Miscenko⁴¹ suggested the presence of a surface-potential, $\Delta\chi$, in double layer studies. A formulation of the water layer at an electrode solution interface in terms of a dipole layer, was first formulated quantitatively by Bockris and Potter³⁵ in connection with the interpretations of pH effects in the hydrogen evolution on Ni. They were the first to introduce a field dependent contribution to an electrode potential from the oriented water dipoles. The water dipole model was used by Bockris and Conway³⁶ (1958) to examine double layer properties with respect to the dependence on frequency of the double layer capacity. Mott and Watts-Tobin⁶ (1961) picked up the concept of Bockris and Conway⁶ (1958) ("wagging" dipoles), and suggested a two-state model for the water-electrode interaction to predict the hump on the capacity potential relations. Correspondingly, MacDonald³⁷ (1959) suggested a treatment of the water layer, assuming all orientations of the water molecules to be equally probable, to explain the hump on the capacity-potential relationship. MacDonald³⁸ (1960) and MacDonald and Barlow²³ (1962) qualified the model of the water layer proposed by MacDonald³⁷ (1959). However, both Mott and Watts-Tobin²³ (1962) omitted the water-water repulsion, i.e., treated the layer as if it were a gas layer.

BDM picked up the two state model proposed by Mott and Watts-Tobin⁶ (1961) and introduced dipole-dipole repulsion energy. They showed that a two-state model was needed to give the parabola observed in $\theta_{org} - q_M$. Taking the repulsion energy into account helped BDM to observe the fact that dipole reorientation may not make significant contributions to the hump, because the dipole capacity was too large to

have a significant effect. However, BDM showed the importance of the dipole reorientation (reduced in magnitude by water-water interactions) in calculating the surface potential as well as in organic adsorption.

BDM showed that the hydration shells of the cations must be outside the water layer. A layer of oriented water dipoles lies between the electrode and the hydrated cations. (Cf. Watts-Tobin, Mott and Parsons²).

BDM's proposal that ionic adsorption isotherms were better calculated on a single imaging theory was independent of Levine, Bell and Calvert²⁸ (1962) who had developed the multiple imaging isotherm. Another approach, more or less similar to the multiple imaging approach of Levine, Bell and Calvert²⁸, but using a hexagonal lattice model was made by Barlow and MacDonald⁴² (1964), which yielded results very much similar to the results obtained by Levine, Bell and Calvert²⁸.

The approach to explain the capacitance hump in the BDM model had an antecedent in the work of Devanathan⁴⁰ (1954), who had shown that:

$$\frac{1}{C} = \frac{1}{K_{M-2}} = \left(\frac{1}{K_{M-2}} - \frac{1}{K_{M-1}} \right) \frac{dq_{CA}^-}{dq_M}.$$

However, Devanathan did not relate q_{CA} to q_M as was done, and compared with experiment, by BDM.

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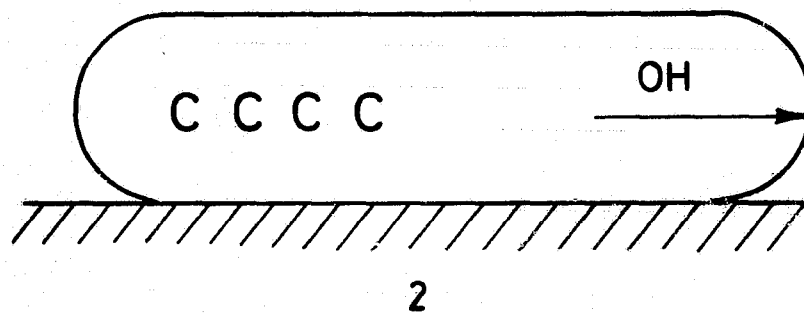
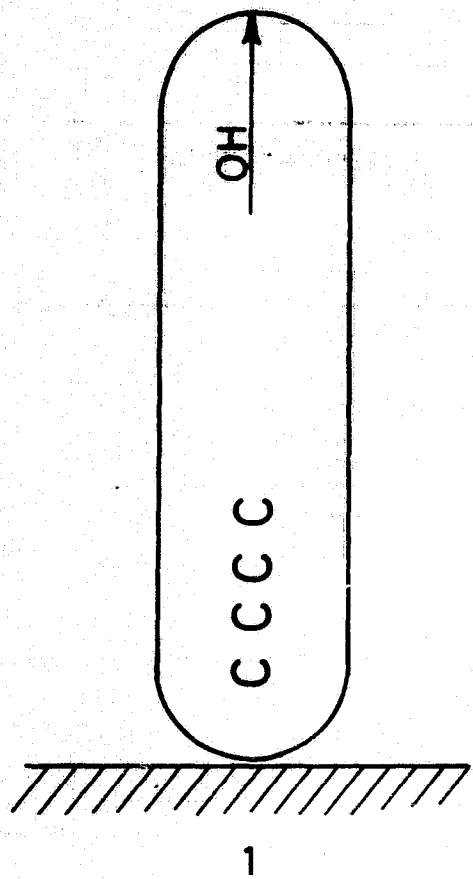


Figure 1.

ANNOTATION FOR FIGURE

Figure 1. Adsorption of organics on electrode:

- (1) Up position - organic dipole in diffuse layer.
- (2) Flat position - organic dipole on electrode surface.

QUANTUM MECHANICAL FORMULATION OF ELECTRON TRANSFER RATES

QUANTUM MECHANICAL FORMULATION OF ELECTRON TRANSFER RATES

Formulation of electron transfer rates in solution and at electrodes has for long been carried out in terms of continuum theory of dielectrics^{1,2}. Some displacement, only recently defined, in the solvent causes the potential energy of the ion concerned to change to a value suitable for the acceptance of an electron, in a radiationless transfer process. The displacement of the solvent has been taken as simple harmonic, and a detailed model has been suggested³. A classical libratory movement of the solvent interacts electrostatically with the ion. Certain long range fluctuations in this energy, rather than the thermally activated vibration-rotation levels involving short range interaction in the ion solvent complex, give rise to the energy states in the ions to and from which electrons transfer.

Two reasons have been advanced³ for the concept that thermally activated vibration-rotation levels usually considered in solution reaction do not take part in an electrode reaction.

First, in electrochemical reactions, variation of electrode potential is brought about by effecting a change of excess charge on the electrode from an outside source, thus causing the Fermi level to change by up to 1eV. Regarding the H_3O^+ levels as only those of vibration, there would be a gap of about 0.5 eV between levels available for the acceptance of electrons. The rate-potential relation is, however, a completely smooth one. Hence, available levels for the relevant quantum transition must be produced by some other means.² This argument, however, neglects rotational levels between the vibrational levels in H_3O^+ (ref. 4), and the considerable line broadening in the spectrum of

H_3O^+ caused by the introduction of solvent⁵. Schiffer and Hornig⁶ interpreted line broadening of the O-H bond, and enhanced Fermi resonance in water, by assuming a classical distribution for free water molecules giving rise to a Boltzmann distribution for the energy of the O-H bond. Similar arguments may be applied to the O-H⁺ bond in water as well.

Second, it has been suggested⁷ that there is an insufficient number of thermal states to sustain charge transfer reactions.

The following analysis shows, however, that this supposition is not supported by considerations of the Boltzmann distribution in solution to experimental activation energies. Thus, the rate of the proton discharge reaction can be written as

$$i = F \cdot \frac{kT}{h} \cdot C_{\text{H}_3\text{O}^+} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}$$

$$= F \cdot \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot N_{\text{H}_3\text{O}^+}^\ddagger$$

where $N_{\text{H}_3\text{O}^+}^\ddagger$ is the number of H_3O^+ ions having sufficiently energetic rotation-vibration levels for radiationless transfer. For the proton discharge reaction on Hg from acid solution, $i_0 \approx 10^{-11}$ amp cm^{-2} , $C_{\text{H}_3\text{O}^+} \approx 10^{13}$ molecules cm^{-2} , and $\Delta S^\ddagger \approx -10$ e.u. (estimated by Temkin⁸ and by Bockris and Sen, unpublished). Thus, $N_{\text{H}_3\text{O}^+}^\ddagger \approx 10^{-3}$ molecule cm^{-2} . For $\Delta H^\ddagger \approx 20$ kcal mol^{-1} (Conway⁹), the number of particles in the second vibrationally excited levels is about 2×10^{-2} molecules cm^{-2} - sufficient to sustain the reaction.

Thus, participation of thermally activated states in electrode reactions is likely¹⁰⁻¹². The fact that solvent fluctuation is unlikely

to be a dominating cause of activation in electron transfer reactions is shown by the following. (1) If one compares the "experimental" standard free energy of activation for a large number of redox reactions in solution with what is calculated on the assumption that solvent fluctuation is the preferred mechanism, there is little correspondence between the two figures¹³. (2) In electrode reactions, the logarithm of the rate is proportional to the overpotential applied. This relation does not follow from the theory of solvent fluctuations, which indicates a continuous curved relation between $\log i$ and overpotential¹³. (3) The polaron theory has been used to estimate the electrostatic fluctuation energy. Polaron theory is applicable in solid lattices, and its applicability to liquids is questionable^{12,14}, and involves correction factors, knowledge of which is not readily available². (4) Direct evidence for the partial nature of the contribution of the continuum energy considerations to charges in solution has been offered by Fueki et al⁷. For energy changes of hydrated electrons, approximately half comes from the continuum electrostatic energy, the rest from the first layer of water molecules around the cavity of the electron, a contribution entirely neglected in the electrostatic fluctuation model. (5) The reorganization energy in the solvent fluctuation models has been given by the Born-Landau equation. The derivation of this equation involves the electronic adiabatic approximation, but Jortner¹⁵ points out that such an approximation on polar liquids, where the binding energy of the solvated electron (about 1.7 eV) and that of the medium electron (about 4eV) are of the same order of magnitude, is not applicable.

The above discrepancies do not mean that some contribution from electrostatic solvent fluctuation does not exist. It is necessary to compare the probability of having electrostatic fluctuations of suitable energy with that of activated vibrational levels of the same energy. Thus, we consider an ion surrounded by N dipoles. The probability of the dipoles having an angle between θ and $d\theta$ with the ion at a distance of R and $R + dR$ is given as

$$P_i = \frac{\frac{3}{2r_\omega^3} \exp\left(\frac{e\mu_{\text{eff}} \cos\theta}{\epsilon_S R^2 kT}\right) R^3 dR \sin\theta d\theta}{\int_0^\pi \int_{r_i}^\infty \frac{3}{2r_\omega^3} \exp\left(\frac{e\mu_{\text{eff}} \cos\theta}{\epsilon_S R^2 kT}\right) R^2 dR \sin\theta d\theta}$$

where r_ω is the radius of a water molecule, r_i that of an ion plus the diameter of a water molecule, and μ_{eff} , following Kirkwood, is the effective dipole moment of the water dipoles caused by the presence of interactions among the water molecules themselves. Using classical statistical mechanics, the mean square deviation of the energy due to fluctuation, σ^2 , can be evaluated to give

$$\sigma^2 = \langle E^2 \rangle - \langle E \rangle^2 = 0.01 \times 10^{-24}.$$

Since σ^2 is small compared with $\langle E \rangle^2$, the probability of having a fluctuation of 20 kcal mol^{-1} above the average energy can be calculated using a Gaussian distribution. It is 10^{-41} . The corresponding probability of having an activated vibrational state of 20 kcal mol^{-1} is 10^{-15} .

Thus the widely acceptance of the solvent fluctuation model for charge transfer reactions should be modified. Thermally activated states, as well as electrostatic fluctuational contributions should be counted. For the slower reactions, the solvent fluctuations do not seem to contribute significantly to the activation process.

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MECHANISM OF ACTIVATION IN ELECTRON TRANSFER IN SOLUTION

MECHANISM OF ACTIVATION OF ELECTRON TRANSFER IN SOLUTION

The velocity of electron transfer between a redox couple¹⁻² or between an electronic conductor and an ion in solution⁴ has been discussed in terms of the Landau-Born⁵ expression for the "electron solvation energy" in solution (the continuum solvent activation model). It is supposed⁶ that the charged particles receive energy from the classical librations of water molecules in a region of a few hundred Å around the ion, in both the initial and final states. The energy transferred from these librators creates a situation in which a radiationless electron transfer can occur.

Acceptance of this model leads to several discrepancies with experiment. (1) Experimentally, the relation between logarithm of the rate of a redox reaction and its overpotential is linear over several decades⁷; this fact is not predicted, even for small regions of potential, by the continuum solvent activation model (Fig. 1); (2) the free energy of activation for redox reactions in solution, predicted by the theory, bears little resemblance to experimental observations (Fig. 2a, b); (3) a piece of evidence in favour of the continuum solvent activation theory is that it predicts the rate constants for the heterogeneous reaction from a knowledge of the homogeneous one. This only involves⁸ the concept of the additivity of the reorganization energy term. This fact is, however, not predicted only by the continuum solvent activation model but also arises from other models of activation where the interaction between the reactants is small.

There are several reasons for the discrepancy between the continuum solvent interaction theory and experiment. (1) In the continuum solvent activation theory the change in the energy of the ion in solution

leading to the activation required for charge transfer is governed only by the interaction of the ion with the solvent, treated as a dielectric continuum. This puts out of consideration the inner solvation sphere of the ion⁶. Such a model might be true, as a first rough approximation, for ions large enough to have no primary solvation sheath attached to them, as is clear from Fig. 2a. For reactions involving aquo-complexes, however, it is the oriented water molecules in contact with the ion which contribute most of the solvation energy of the ion and which therefore should make a significant contribution to the energy of activation of the ion. Consequently the use of the continuum solvent model to calculate energy changes is inappropriate for such reactions. This is also evident from Fig. 2b. In such cases, the inner sphere contribution becomes the dominant factor. This is supported by the demonstration by Kevan et al⁹ that the energy of a solvated electron is not represented by a continuum Born-type expression but principally by nearest neighbour interaction with water dipoles. The continuum estimate is in error by about 2 eV.

(2) It is implicit in the continuum solvent activation model¹⁻⁴ that the energy of the perturbations which gives rise to the activation of the ion is proportional to the square of a displacement within the solvent. This might indeed be so if the activators were, for example, water librators at relatively large distances (for example 50 Å) from the ion. It is not a likely representation of the energy-distance relation if the nearest neighbour interactions of the charge in solution are taken into account, because the vibrations and rotations relevant contain anharmonicity. It is this lack of anharmonicity in the classical theory which is the origin of the poor prediction of the relation between log

rate and overpotential. If such anharmonicity is taken into account there is excellent agreement between theory and experiment (that is, there is linearity between $\log i$ and η) for many decades^{8,10}.

(3) One of the reasons which has been given⁶ for neglecting the inner sphere contributions in the continuum solvent model was the quantal character of the vibrations in the inner sphere. As a recent spectroscopic discussion of H_3O^+ has shown, however, rotational motions in solution are classical¹¹ and there is usually strong coupling between vibrational and rotational motion; the energy of the inner sphere may, therefore, be activated classically. Together with the classical states induced by the Bornian contribution to the total solvation energy of ion, the total energy of the initial state will in effect be classical. This has an important consequence because no discontinuity in the $\log i$ - η relations is seen although the structure can be analysed to show up energy changes of 0.001 eV.

One of the remaining uncertainties concerns very large ions: does the Landau-Born expression play an important part as a limiting case - that is, if the ion is so large that there is no orienting structure around it? For this to be so, it is necessary to assume the applicability of the theory of polarons in water; this is, however, unlikely^{9,12}.

The activating modes in most of the electron transfer reactions are therefore not primarily the non-equilibrium polarizations of the solvent treated as a continuum.

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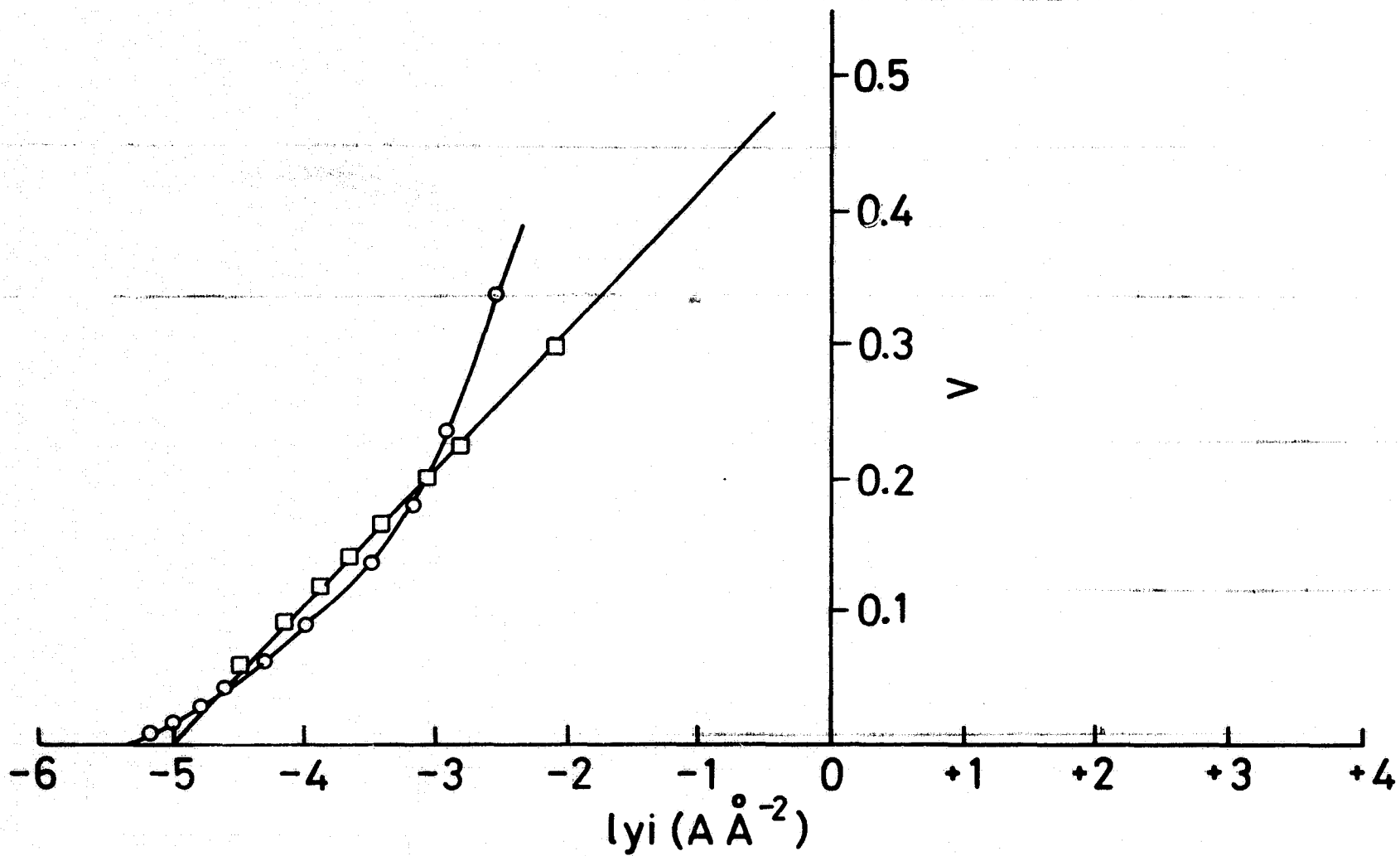


Figure 1.

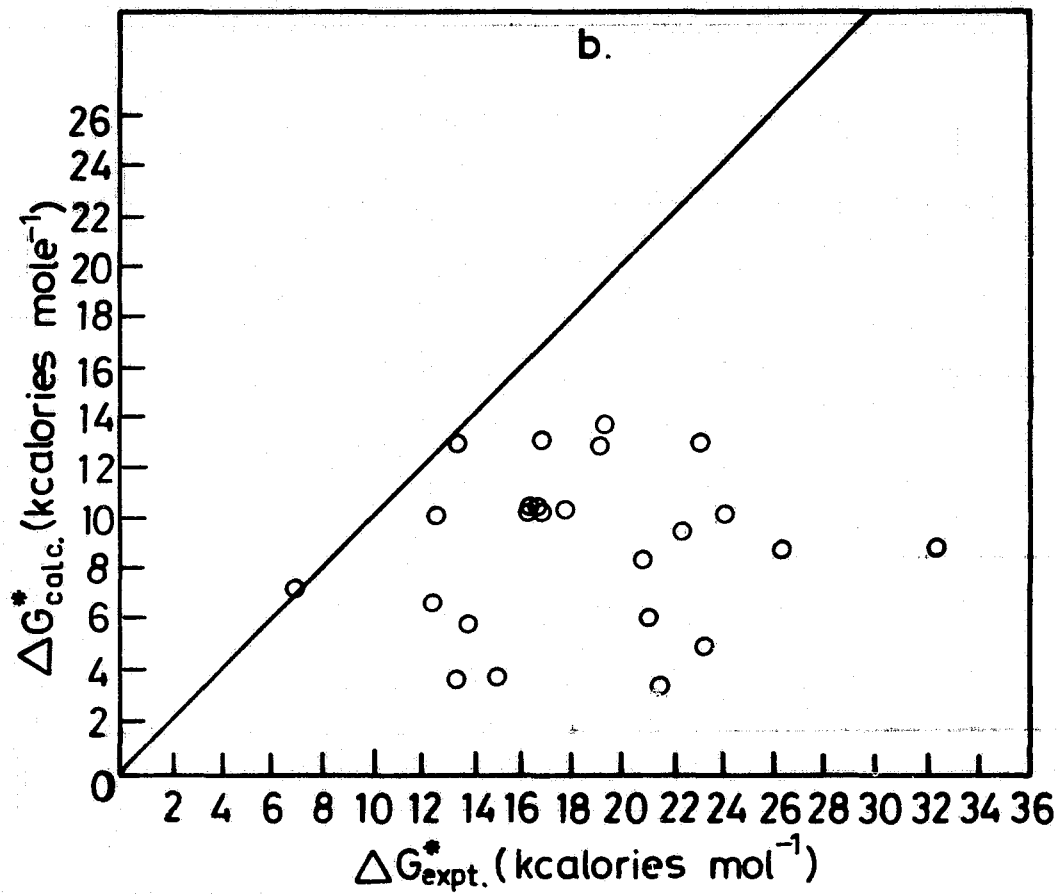
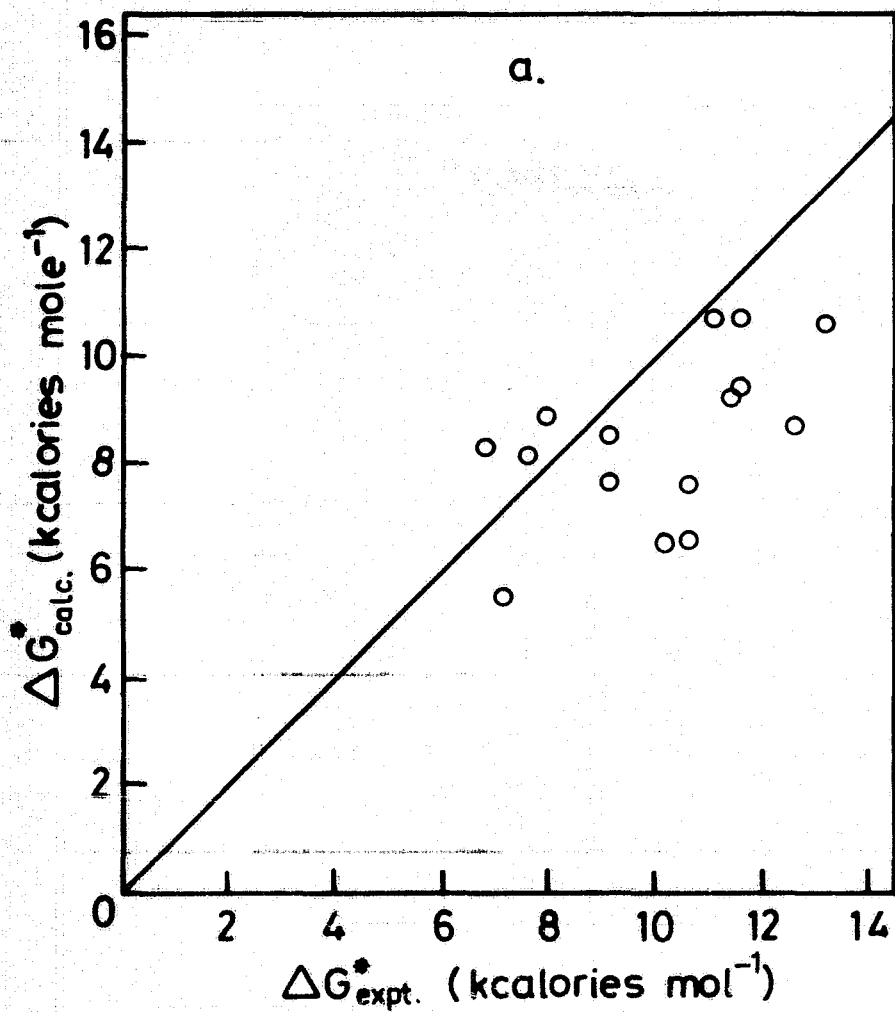


Figure 2.

ANNOTATIONS FOR FIGURES

Figure 1. Tafel line for redox reactions. ($\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$). -, Theory;
 \square , experiment.

Figure 2. a, Plot of ΔG^*_{calc} against ΔG^*_{expt} for electron transfer reactions involving reactants with ligands other than water or ammonia; b, plot of ΔG^*_{calc} against ΔG^*_{expt} for electron transfer reactions involving reactants with water or ammonia molecules as ligands.

ON QUANTUM ELECTROCHEMICAL KINETICS

ON QUANTUM ELECTROCHEMICAL KINETICS

Abstract

A critical estimation is made of the theory of electrochemical kinetics in terms of two models of activation, thermal and electrostatic. It has been shown that the electrostatic model cannot predict the linearity of a Tafel line and also the constancy of symmetry factor β with overpotential and the relation of rate constants k_{hom} and k_{het} does not diagnostically support the electrostatic model.

A quantum mechanical derivation is given to show the consistency of the time dependent perturbation theory with the GAMOW equation for the time dependent barrier concerned in charge transfer.

1. HISTORICAL

Few examples^{1,2,3} are available where an attempt has been made to investigate the quantum mechanical aspects of reaction rates, even in the gas phase. However, quantum mechanical aspects of electron transfer reaction in solution were first discussed by GURNEY⁴ in 1931: it was one of the first topics in Chemistry to receive quantal discussion.

The Gurney⁴ theory was developed by Butler⁵, Christov⁶, Gerischer⁷ and Bockris et al⁸.

The basic aspect of this type of model is that there is a thermal equilibrium between the solvated ions and the solution. A Boltzmann distribution is assumed to give a population of excited vibrational states of the ion, and the rate of the electron transfer reaction in the product of the probability of a quantum mechanical transition (usually of an

electron) and that of the probability of finding a suitable acceptor (or donor) level in the ion. This model will be referred to as the thermal activation model.

Another model originates with Libby⁹, who suggested that, in a redox reaction, the energy change during electron transfer could be expressed as the difference between the Born solvation energies of the initial and final states (but see ref. 10). Weiss (1954)¹¹, followed by Hush (1968)¹² and Marcus (1959)¹³ developed a view in which the optical polarisation associated with a fast electron transition was the principal part of an expression for the heat of activation. In 1965 Marcus¹⁴ developed a more detailed model, which took into account contributions to activation from the inner solvation sheath. The former approach, - that based on the Born equation, - has continued to be developed by Levich¹⁵, with Dogonadze¹⁶ and Kuznetsov¹⁷, with explicit stress upon the validity of the application of the Born equation and the rejection of contributions by the inner shell of activation. This latter model (that which stresses the Born equation) will be referred to here as the continuum electrostatic approach.

Until 1970, the physical meaning of the continuum electrostatic view was not differentiated from that of Weiss¹¹, Hush¹² and Marcus¹³. It did not contain a molecular-level description of how energy was transferred from the solvent to the entity to receive charge (which must exist in an activated state at the moment of transition). In 1970, Levich¹⁸ suggested a molecular model which sought to rationalise the continuum electrostatic view in terms of fluctuation theory.

In this report, we would like to make a comparison of the two models*.

II. THE TWO MODELS

1. Description of the Models

The following is common to both models:

(a) A radiationless electron transfer is assumed. Therefore, one calculates a condition for setting up equal electronic energy states on the electrode and the solution side of the barrier, so that electron transfer can occur from the state E_F , the Fermi level in the electrode, to a state of the same energy in the solution.

(b) As with the consideration of the quantum mechanical transitions in reactions, the Born-Oppenheimer approximation is invoked to separate the fast moving electronic coordinate and the coordinates of the heavy particle, e.g., at H_2O^+ ion, or the solvent.

(c) In considering the hydrogen evolution reaction, both approaches consider the quantum mechanical aspect of a proton leaking through the barrier. But in the continuum electrostatic approach, the transfer of a heavy particle is pictured as occurring by means of a "quantum mechanical transition" of the whole system. In the development of the thermal view the transfer of heavier particles over the barrier is taken into account.

* Importance of the field gains because many biophysical reactions probably involve interphasial charge transfer¹⁹.

We now describe the differences.

(i) Thermal Model

The model assumes that the H_3O^+ ion is in thermal equilibrium with the surrounding solvent and there is a Boltzman distribution of electronic energy levels in the ion and its solvent shell which provides a distribution of levels to correspond to the varying electronic level which occurs as the potential of the electrode is changed. Therefore, there must be some states in the H_3O^+ ion which possess an energy to match the Fermi level of electrons in the electrode. It is to these states that electron transfer from the metal occurs without gain or loss in energy.

In this approach, the permeability of the barrier to protons is taken into account. Depending upon the energy level in the proton, at penetration, there is a probability of electrons being in the same level in the metal, whereupon a transition of the electron to the penetrated protons occur. Some protons will also go over the barrier. For heavy ion transfer, all the transitions will be over the barrier. For these, the quantal character of the electrode reaction will be (effectively) restricted to the electronic transition.

An electrostatic contribution to the energy of the initial state (ion in the double layer and electron in the metal) was made explicit by Parsons and Bockris²⁰ and Conway and Bockris²¹. They took into account the electrostatic energy of the ion in defining the electron energy level in the initial state. These energy contributions were divided into chemical, ion-dipole and Born terms. They were thought of as contributions to the energy of the system at equilibrium. Vibrations of the inner solvation sphere will, however, change the radius term in the Born equation and can

produce a continuum electrostatic fluctuation, in addition to whatever other fluctuations may arise in the electronic energy of the ion due to the librations of nearest neighbour dipoles.

(ii) Electrostatic Continuum Model

This model differs radically from the basic model used in the theory of activation in kinetics, where the small number of excited bonds are the medium of the reaction. In the electrostatic continuum model, for a bond for which $h\nu \gg kT$, the occupancy of the level (in the thermal distribution) is too small at room temperature that it does not play a part in the reaction. But species have to be excited. To achieve this, the reacting ion is pictured as existing in a dielectric continuum, and dielectric polarization fluctuations in the continuum are suggested as the cause of fluctuations in the energy of the reacting species.

Levich¹⁸ suggests that the fluctuating particles are water molecules, i.e., dipoles, undergoing librations in solution. They have a frequency of about 10^{11} sec^{-1} , so that for these $\frac{h\nu}{kT} \ll 1$, and they behave classically at room temperature*. These librators produce longitudinal polarization waves and give rise to electrostatic fluctuations in the energy of the ion. Since a large number of librators are needed for the activation**

* 10^{-11} sec is the Debye relaxation time in water. This has been attributed to water dipole librations by Levich^{15,16,18}.

** Levich¹⁸ calculates the approximate number in the following manner: If E_a be the activation energy, and each dipole has the capacity of contributing an amount of energy not exceeding its own energy $h\omega_0$, then if N dipole takes part in creating the reaction situation, the value of N is given as:

$$N \gtrsim E_a / h\omega_0$$

For $E_a \sim 0.5 \text{ ev}$, the $N \gtrsim 10^3$.

However, using $\omega_0 = 10^{11}$, the frequency quoted by Levich for the librators in water,

$$h\omega_0 \approx \frac{1}{100} kT.$$

Thus, the majority of librators would possess about 100 quanta, in which case the number of particles needed for activities would be about 10. Whether a continuum polaron concept can be applied to this small number must be questioned.

possess, it is necessary that these longitudinal waves are in phase, i.e., the oscillators librate in phase to create a standing wave, for, otherwise, sufficient energy cannot be transferred to the ion. Thus, the concept of the polaron theory developed for solid crystals is used to describe the activation process. In this way (though not explicitly), it is suggested that energy pulses of the order of 1 ev. reach the ion, placing it thus momentarily at an energy level at which radiationless transfer can occur.

Second-order time-dependent perturbation theory is used to solve for the quantum mechanical transition probability of the electron and for the proton in the hydrogen evolution reaction.

2. The Rate-Overpotential relation according to both Models*

Both the models start off from the fundamental equation, which gives the rate of an electron transfer reaction as**:

$$i = eC_s \int_s \int_x n(\epsilon_f) \rho(\epsilon_f) W_{if}(\epsilon_f) d\epsilon_f dx, \quad (1)$$

where i is the current per sq. cm. and gives in fact the rate of the electron transfer reaction.

The main difference in approach is in the calculation of the transition probability, $W_{if}(\epsilon_f)$. We will examine the methodology in a

* For list of symbols, see end.

** The double integral is annulled in the following simple treatment by taking the electrons only from the Fermi level and the distance of the acceptor states at the outer Helmholtz plane.

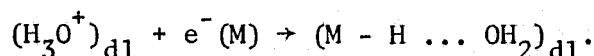
simplified way to show the essence of each model.

(a) The Thermal Approach

One may consider that electron transfer reactions are adiabatic, i.e., the electronic motions are faster than the motions of the heavy particles (the ions). The probabilities of electron transfer (P_T), and of attaining suitable acceptor states ($P_{H_2O^+}(\epsilon)$), are hence independent. The transition probability (taken here, for simplicity, as occurring only from the Fermi level) is:

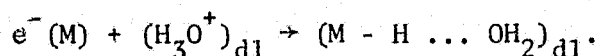
$$W_{if}(\epsilon_f) = P_T P_{H_2O^+}(\epsilon) \quad (2)$$

The problem is to evaluate these two probabilities separately. For the hydrogen evolution reaction, the rate-determining step may be chosen for the sake of discussion as that corresponding to:



The potential energy profile will be as shown in Fig. 1.

The vertical transition (see Fig. 1) AB corresponds to the process:



i.e., of taking an electron from the Fermi level of the metal to an H_3O^+ ion in its ground rotation-vibration state, with no change in the proton-coordinate, d . The energy change of the system for this vertical process is, say, $\Delta H_0(e)$, (Fig. 1). Such a transition for an H_3O^+ ion not in its ground state will be accompanied by an energy change $\Delta H_0(e)$. Eventually, at the intersection point X of curves "a" and "b" in Fig. 1, $\Delta H_0(e) = 0$

and electron tunneling from the metal to the proton becomes possible*.

Since the thermal model assumes that a Boltzman distribution exists between the various vibrational-rotational energy states of the $\text{H}^+\text{-OH}_2$ ion, the probability of finding the $\text{H}^+\text{-OH}_2$ ion sufficiently activated, so that its energy will correspond to the intersection point X of Fig. 1, is given by**:

$$P_{\text{H}_3\text{O}^+}(\epsilon) = \exp\left(-\frac{\Delta\epsilon}{kT}\right). \quad (3)$$

From Fig. 1, $\Delta\epsilon$ is a fraction of ${}_0\Delta H_0(e)$,

$$\Delta\epsilon = \beta_0 \Delta H_0(e)$$

where $0 < \beta < 1$.

Hence:

$$P_{\text{H}_3\text{O}^+}(\epsilon) = \exp\left(-\frac{\beta_0 \Delta H_0(e)}{kT}\right). \quad (4)$$

Since:

$$\left({}_0\Delta H_0(e)\right)_{\Delta\phi} = {}_0\Delta H_0(e) + e\Delta\phi$$

we have

$$P_{\text{H}_3\text{O}^+}(\epsilon) = \exp\left(-\frac{\beta_0 \Delta H_0(e)}{kT}\right) \exp\left(-\frac{\beta e\Delta\phi}{kT}\right). \quad (5)$$

* For the h.e.r., the r.d.s. of which is $(\text{H}_3\text{O}^+)_{d1} + e^-(M) \rightarrow (M-H \dots \text{OH}_2)_{d1}$ the point X in Fig. 1 is the point where the equality $I + L - \phi = R + A$ is satisfied (see Bockris and Matthews⁸). Rewriting the above equality in the form $\phi = I + L - R - A$ shows that at the point X the radiationless electron tunneling condition is also satisfied (see Gurney⁴).

** The presentation is heuristic. The quantum mechanical properties of the proton are suppressed, for the sake of simplicity in the presentation of principles. Such properties have been taken into account^{8b}.

The tunneling probability, assuming a square barrier* is:

$$P_T = A \exp\left[-\frac{4\pi\ell}{h}\{2m(E_X - E_F)\}^{1/2}\right]. \quad (6)$$

Hence, the total current, using equation (6), is**:

$$\begin{aligned} i_{\Delta\phi} &= 2eC_8 \frac{4\pi m (kT)^2}{h^3} \exp\left[-\frac{4\pi\ell}{h}\{2m(E_X - E_F)\}^{1/2}\right] \times \exp\left[-\frac{\beta(\Delta H_o(e) + e\Delta\phi_e)}{kT}\right] \\ &\quad \left(\exp - \frac{\beta e\eta}{kT}\right) \\ &= i_o \exp\left[-\frac{\beta e\eta}{kT}\right]. \end{aligned} \quad (7)$$

This is Tafel's law.

(b) The Electrostatic Approach

As mentioned in Sec. IV, the electrostatic approach makes an initial assumption in contrast to theories of activation in collisional kinetics that bonds for which $h\nu/kT \gg 1$ do not take part in the reaction. The activation is effected by classical degrees of freedom. Moreover, the ion-solvent interaction in the inner solvation sheath gives rise to the

* Again, the barrier has been taken here as the simplest for heuristic purposes. Christov⁶, and Bockris and Matthews^{8b} discussed the quantum mechanical properties of the proton in terms of Eckert barriers.

** E_F varies linearly with overpotential. However, E_X also varies linearly with overpotential. Thus, as the overpotential changes, the state in H_3O^+ to which an electron is transferred changes by the same amount and the height of the electron transfer barrier remains independent of potential. There will be a change in field strength in the double layer as a function of overpotential. However, the expected changes (say, a doubling of field strength) can be shown^{8c} to have a negligible effect on the shape and height of the electron transfer barrier.

inequality $h\nu \gg kT$. Thus, the number of particles in the higher energy states is few. This is usual in any reaction kinetic situation. In the present theory, it is assumed that there are too few of such higher energy bonds to be of interest in the process. The suggestion is that classical harmonic librators in the bulk of the solvent produce (by means of long range electrostatic interactions) fluctuations in the electronic energy levels of the ion, to give it its required energy for a quantum mechanical transition.

Thus, the potential energy profile in the initial and final state are essentially produced from the intersection of two harmonic potential wells, as shown in Fig. 2.

Corresponding to the heuristic presentation given of the thermal model, we regard the transition probability as the product of the electron transfer probability and the probability of the acceptor state attaining the level where a radiationless electron transfer takes place. Thus:

$$W_{if}(\epsilon_f) = P_T P(\Delta\epsilon), \quad (8)$$

where P_T now is the transmission coefficient, or electron transfer probability, and $P(\Delta\epsilon)$ is the probability that the acceptor state is in its activated configuration ready to accept an electron. To evaluate $P(\Delta\epsilon)$, consider the PE profile of Fig. 2. Putting the equation of the parabolas in the form^{24*}:

$$\left. \begin{aligned} U &= k(q - d)^2 \\ \text{and} \\ U - Q &= kq^2 \end{aligned} \right\}, \quad (9)$$

* The assumption of simple harmonic behaviour arises because the displacement of each oscillator involved in contributing to the activation of the ion is only about 10^{-3} ev.

where k is a force constant. For the purpose of simplification, we have set the k 's for the two parabolas to the same.

At the intersection point, we can therefore write:

$$kd^2 - kdq^1 - Q = 0. \quad (10)$$

A reorganizational energy, E_S , can be defined as the energy difference between the ground state of the reactant and the point corresponding to its displacement q to overlap the ground state of the other oscillator. Hence, by definition (Fig. 2):

$$E_S = kd^2. \quad (11)$$

Therefore, from equation (10):

$$E_S + Q + 2kq'd = 0$$

or

$$q' = -\left(\frac{E_S + Q}{2kd}\right).$$

Hence,

$$E_{\text{act}} = kq'^2 = \frac{(E_S + Q)^2}{4E_S}. \quad (12)$$

Since the potential energy profiles are made up of classical oscillations, the Boltzman distribution is valid.

Therefore:

$$P(\Delta\epsilon) = \exp\left(-\frac{E_{\text{act}}}{kT}\right) = \exp\left(-\frac{(Q + E_S)^2}{4E_S kT}\right). \quad (13)$$

Thus,

$$\begin{aligned} i &= eC_S \rho_o P_T \eta(\epsilon_f) \exp\left(-\frac{(Q + E_S)^2}{4E_S kT}\right) \\ &= A \exp\left[-\left(\frac{E_S}{4kT} + \frac{Q}{2kT} + \frac{Q^2}{4E_S kT}\right)\right]. \end{aligned} \quad (14)$$

The potential dependent part is lumped in Q , since:

$$Q = J_{in} - J_{fn}$$

where J_{in} and J_{fn} are the ground state energies of the initial and final states. Therefore, we can write:

$$Q = Q_0 + e\eta.$$

If, in equation (14), $Q^2 \ll 4E_S kT$, then:

$$\begin{aligned} i &= A \exp \left[- \left(\frac{E_S}{4kT} + \frac{Q_0}{2kT} + \frac{e\eta}{2kT} \right) \right] \\ &= A' \exp \left[- \frac{e\eta}{2kT} \right]. \end{aligned} \quad (15)$$

Thus, we obtain the Tafel equation.

However, to obtain this result $Q^2 \ll 4E_S kT$. This is not usually true. Thus, the electrostatic continuum model does not give a linear Tafel line. There are no regions on the overpotential-log current relation which should be linear, in contradistinction to experiment.

3. Differences between the Two Models

The main difference between the two models is in the mode of energy communication between the solvent and the ion.

In the electrostatic continuum view, vibration-rotation levels due to the thermal equilibrium of the reacting species are neglected. Electrostatic fluctuations from long range interactions of a large number of dipoles (see footnote) are envisaged. The electrostatic contribution from librations of the inner solvation shell is neglected.

The reason put forward¹⁸ for the neglect of vibrations of the inner solvation sheath, is that, since the ion-solvent interaction of the ion is large, the thermal movements of the solvent molecules in the inner solvation sheath $h\omega/kT \gg 1$. It seems to be suggested that, because of the small excited to higher states, the effect of vibrational activation of the inner solvent sheath can be neglected (See Section IV).

The other main difference between discussions in terms of thermal and electrostatic activation is in the treatment of the transition probability. In the electrostatic continuum view, the treatment has not been explicitly made, but it is suggested that it be made by means of time-dependent perturbation theory. In the thermal view, a WKB approximation is applied to obtain a one-dimensional probability of passage through a barrier (Section IV).

III. COMPARISON WITH EXPERIMENT

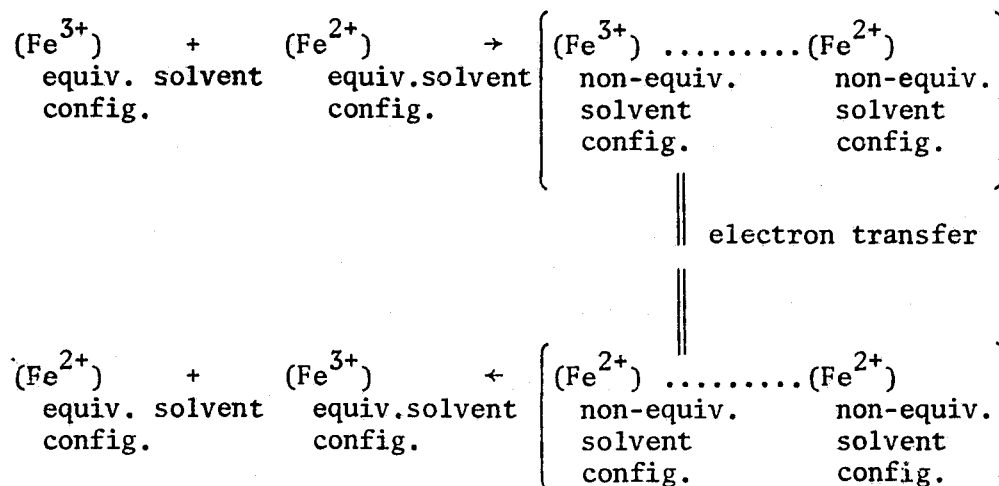
1. Relation between k_{het} and k_{hom} .

An argument which has been used to support the continuum electrostatic theory^{25,13} is that the rate constant for the heterogeneous reaction can be predicted from the rate constant for the homogeneous reaction. The prediction is:

$$\left(\frac{k_{\text{hom}}}{z_{\text{hom}}} \right)^{1/2} = \left(\frac{k_{\text{het}}}{z_{\text{het}}} \right), \quad (16)$$

where k_{hom} and k_{het} are the rate constants for the exchange reaction in solution (e.g., $\text{Fe}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+}$) and at an electrode (e.g., $\text{Fe}^{3+} + e(\text{M}) \rightarrow \text{Fe}^{2+}$). Let us derive this equation from the most general assumptions.

Consider the homogeneous reaction $\text{Fe}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+}$
 as proceeding along the path:

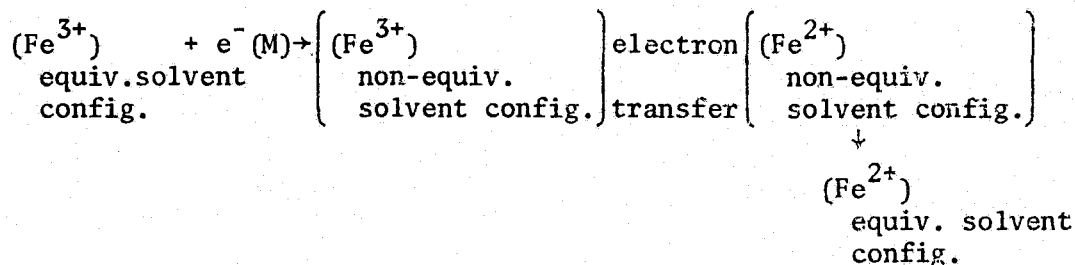


The free energy of activation may then be written as:

$$\Delta F_{\text{hom}}^* = \left[\left(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}} \right) - \left(\Delta F_{(\text{Fe}^{3+})_{\text{esc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \right) \right] \quad (17)$$

where $\left(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}} \right)$ is the free energy of the activated state and $\left(\Delta F_{(\text{Fe}^{3+})_{\text{esc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \right)$ is the free energy of the initial state.

For the corresponding heterogeneous reaction $(\text{Fe}^{3+} + e^-(M) \rightarrow \text{Fe}^{2+})$, proceeding according to the path:



The activation free energy for the forward and backward reaction can then be written as:

$$\Delta F_{\text{het}}^{\rightarrow} = \frac{1}{2}(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) - \Delta F_{(\text{Fe}^{3+})_{\text{esc}}} \quad (18)$$

and

$$\Delta F_{\text{het}}^{\leftarrow} = \frac{1}{2}(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) - \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \quad (19)$$

where $\frac{1}{2}(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}})$ is the free energy of the activated state and $\Delta F_{(\text{Fe}^{3+})_{\text{esc}}}$ and $\Delta F_{(\text{Fe}^{2+})_{\text{esc}}}$ are free energies of the initial state.

The two activated states are in resonance and have equal energies. Hence:

$$\frac{1}{2}(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) = \frac{1}{2} \times 2\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} = \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}}$$

Similarly,

$$\frac{1}{2}(\Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} + \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}) = \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}}$$

Hence:

$$\left. \begin{aligned} \Delta F_{\text{het}}^{\rightarrow} &= \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{3+})_{\text{esc}}} \\ \Delta F_{\text{het}}^{\leftarrow} &= \Delta F_{(\text{Fe}^{2+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \end{aligned} \right\} \quad (20)$$

Moreover, at the equilibrium potential, and equal concentration of reactants and products:

$$\overset{\rightarrow}{\Delta F_{\text{het}}^*} = \overset{\leftarrow}{\Delta F_{\text{het}}^*} \quad (21)$$

Now, we can rewrite equation (17) as:

$$\begin{aligned} \Delta F_{\text{hom}}^* &= \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} = \Delta F_{(\text{Fe}^{3+})_{\text{esc}}} + \Delta F_{(\text{Fe}^{3+})_{\text{nesc}}} - \Delta F_{(\text{Fe}^{2+})_{\text{esc}}} \\ &= \overset{\rightarrow}{\Delta F_{\text{het}}^*} + \overset{\leftarrow}{\Delta F_{\text{het}}^*} \end{aligned} \quad (22)$$

So, at the equilibrium potential,

$$\Delta F_{\text{hom}}^* = 2\Delta F_{\text{het}}^* \quad (23)$$

But:

$$\left. \begin{aligned} k_{\text{hom}} &= z_{\text{hom}} \exp\left(-\frac{\Delta F_{\text{hom}}^*}{RT}\right) \\ \text{and} \\ k_{\text{het}} &= z_{\text{het}} \exp\left(-\frac{\Delta F_{\text{het}}^*}{RT}\right) \end{aligned} \right\} \quad (24)$$

Hence:

$$\left(\frac{k_{\text{hom}}}{z_{\text{hom}}}\right) = \exp\left(-\frac{\Delta F_{\text{hom}}^*}{RT}\right) = \exp\left(-\frac{2\Delta F_{\text{het}}^*}{RT}\right) = \left(\frac{k_{\text{het}}}{z_{\text{het}}}\right)^2$$

Thus:

$$\left(\frac{k_{\text{hom}}}{z_{\text{hom}}}\right)^{1/2} = \left(\frac{k_{\text{het}}}{z_{\text{het}}}\right)$$

No assumptions or models have been used in this derivation.

Thus, relation (16) does not support particularly the continuum electrostatic view.

2. Predictions of the Free Energies of Activation from a Continuum

Electrostatic Theory.

The free energy of activation, ΔF_{calc}^* is given according to the continuum electrostatic view¹⁸ by:

$$\Delta F_{\text{calc}}^* = \frac{(E_S + Q)^2}{4E_S} \quad (25)$$

where

$$E_S = \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{\epsilon_{\text{opt}}} - \frac{1}{\epsilon_{\text{stat}}} \right) (ne)^2 .$$

ΔF_{calc}^* were computed for 52 reactions, including both the electron exchange (e.g., $\text{Fe}^{*2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{*3+} + \text{Fe}^{2+}$) and usual electron transfer (e.g., $\text{Fe}^{2+} + \text{Ce}^{3+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{2+}$) reactions. They were made for various ligands as well.

There are few electron transfer reactions for which the temperature dependence of the rate has been studied. One can calculate an "experimental" value for free energy of activation by equating the rate constant (experimentally determined to $Z_{\text{bi}} \exp\left[-\frac{\Delta F_{\text{exp}}^*}{RT}\right]$, where Z_{bi} is the bi-molecular collision number* of the two uncharged species in solution per unit volume, per unit time and is given as¹⁴:

*The equation (26) used for Z_{bi} is valid only for gas kinetic collisions.

Application to solutions would be a drastic approximation. Let us derive a crude Z_{bi} for solutions. Assume a quasi lattice model for a liquid, each reactant A and B being surrounded by N nearest neighbours in a hexagonal array. The time for a reactant to jump to a nearest lattice site is:

$$t(r_{\text{AB}}) = \frac{r_{\text{AB}}^2}{6D_{\text{AB}}} .$$

$$Z_{bi} = \left(\frac{8\pi kT}{m^*} \right)^{1/2} r^2 . \quad (26)$$

Using 10^{11} for Z_{bi} and the experimentally determined k (the rate constant), the experimental ΔF_{expt}^* can be obtained.

The ΔF_{calc}^* is plotted against the experimental ΔF^* value in Fig. 3. There is no general correlation between the prediction of the electrostatic continuum view and experiment. A few points lie close to the theoretically expected line. An attempt was made to categorize the reactions on the basis of the nature of ligands and reconstructed the plots as shown in Fig. 4a and 4b. In Fig. 4a redox couples with CN^- , Br^- , Cl^- and O^- as ligands give results near to those predicted, whereas poor agreement is obtained with ligands like H_2O , NH_3 , dipy, Phen.

The most likely cases in which the electrostatic continuum view would have applicability would be for ions of largest radius. There, a set of water molecules oriented around the ion and remaining attached to it for times much longer than the ions jump time in diffusion "primary solvation", would be unlikely²⁶. The continuum viewpoint might be more correct. Hence, a plot of $\frac{\Delta F_{\text{calc}}^*}{\Delta F_{\text{expt}}^*}$ should tend to unity with increasing radius. Such a test is shown in Fig. 5, and shows the theory to be inconsistent with this test.

3. Variation of β with overpotential and the Tafel relationship from both the approaches

The continuum electrostatic theory predicts that for the h.e.r. in the normal overvoltage region, the transfer coefficient is given as:

$$\beta^* = \frac{1}{2} + \frac{J_{fn'} - J_{in}^0}{2E_S} - \frac{e\eta}{2E_S} \quad (27)$$

Experimentally, it has been found^{27,28} that for h.e.r. the transfer coefficient remains constant over more than 1 ev. From equation (27) this would be so only if $J_{fn'} - J_{in}^0$ (heat of reaction at the reversible potential) = $e\eta$. In Fig. 6 the transfer coefficient β^* , calculated according to the electrostatic continuum theory, varies linearly with overpotential. Using these values of the transfer coefficients for $E_S = 2\text{ev}$, the predicted Tafel line is shown in Fig. 7. There is markedly no linear region at variance with the experimental line.

In the thermal model, β is:

$$B_C = \frac{1}{2} - \frac{1}{2ax_0} \frac{[1 - \{(\langle \Delta H \rangle^* - (1 - \beta)F\eta)/D\}^{1/2}]}{[1 - \{(\langle \Delta H_1 \rangle^* - A_0 + \beta F\eta)\}^{1/2}]} \quad (28)$$

The variation with potential is shown in Fig. 6. The agreement is good.

Using these β values the Tafel line was evaluated using the expression:

$$i = C_H^+ \left(\frac{\pi r^2}{3} \right) \left(\frac{4\pi m_e e_1 kT}{h^3} \right) \bar{w} e \int_{-w}^{+w} \left(1 + \exp \frac{[E - E_1]}{RT} \right)^{-1} \times \exp [-\beta_0 (E_0 - E)/RT] dE \quad (29)$$

The equation was derived by Bockris and Matthews⁸ and solved numerically using a digital computer. The theoretical and experimental lines are shown in Fig. 7. The β stays constant over a wide range of potential, and the Tafel line obtained agrees with experiment quite well.

4. Predictions of the Electrostatic (E) and Thermal (T) Models

| <u>Test</u> | <u>Symbolic Representation</u> | <u>Comments</u> |
|---|---|--|
| 1. (a) The current density is exponentially proportional to the overpotential. | $i = Ae^{\beta\eta}$ | T predicts experiment. E shows continuous curvature. Fig. 7. |
| (b) Variation of β with overpotential. | $(\beta)_{\eta \rightarrow \infty} \rightarrow 0$ | T gives negligible variation over 1.5 V for her. E shows continuous variation. Fig. 6. |
| 2. Magnitude of separation factors on different metals. | $S_{H/T} = 3-20$ | No calculation done on E model. T model reproduces experiment for high η . |
| 3. Variation of the separation factor with potential. | $S_{H/T} = f(\eta)$ | T reproduces $dS/d\eta$ better than E. Fig. 8. |
| 4. For reaction which involves adsorbed intermediates, the current is a function of the heat of adsorption of one of the intermediates involved in the rate-determining step. | $(\log i)_{\eta}^{\infty}$ $f(\Delta H)_{ads}$ | For h.e.r. both models are consistent with experiment. Fig. 9. |
| 5. The rate is a function of the solvent dielectric constant. | $(\log i)_{\eta} = f(\epsilon)$ | Predicted well by T model; and not by E model. Fig. 10. |
| 6. The current density is a function of light. | $(i)_{\nu} = K(v-v_0)^{5/2}$ | Not yet diagnostic ³⁰ . |
| 7. Plot of ΔF^*_{expt} vs. ΔF^*_{calc} . | ΔF^*_{expt} vs ΔF^*_{calc} | No correlation on E theory. Fig. 3. |

The thermal activation model gives a better agreement with experiment than the continuum electrostatic view, particularly in respect to the tests (1a), (1b), (5) and (7). However, this may arise from approximations at present used in the electrostatic continuum model. It is therefore desirable to discuss the likelihood of the models themselves.

IV. CRITICAL CONSIDERATION OF BOTH APPROACHES

1. The Activation Mechanism

The poor current potential relationship obtained from the electrostatic approach arises from the parabolic nature of the potential energy profile. The small perturbations in libratory oscillations of the solvent molecules, far away from the ion, must be harmonic. Since these oscillations activate the ion, the potential energy profile must be harmonic, too. A source of anharmonicity could be the vibrations and librations of the inner sphere dipoles, where there is strong interaction between the ion and the dipole. However, this source of activation is specifically rejected in the continuum electrostatic approach¹⁸.

The mode of activation envisaged by the electrostatic approach involves the fluctuations of about a 1000 dipoles (see Section II) "in phase". If the librations were not in phase, the large number of dipoles needed could not transfer energy to the ion additively at the same instance. Polaron theory in solids, where a system of interacting oscillators are coupled to one another, has postulated such fluctuation⁴⁶. It does not seem to be unreasonable in a solid. However, in a liquid without appreciable periodicity, it is questionable whether the principles of polaron theory can be applied at all³¹. Thus, Nemethy and Scheraga³² showed that in water at any instant the percentage of free water ranges between 20~50%. It is doubtful that such a liquid will produce a significant probability of oscillators in phase.

Even if there is a group of some 1000 dipoles librating in phase and contributing their energy additively to the ion, there would be another (and another) group of 1000 dipoles librating together but in

a different phase. The effects would cancel.

Such a model might be modified to be applicable where there is a highly oriented secondary solvation sheath extending to about 20\AA from the ion. In such a case, librations of the dipoles in the secondary solvation sheath might be in phase, and if it extends to about 20\AA from the ion, the possibility of 1000 dipoles taking part is not unreasonable. However, a recent calculation by Bockris and Saluja²⁶ shows that entropy and heat calculations are difficult to bring into consistency with the experimental values if the water structure is broken past two layers from the ion. Amis³³ has discussed a large structure broken secondary layer. The evidence for it, however, is ambiguous for it rests upon the values obtained for "solvation numbers" from various methods, which are of such ill defined significance.

Coming to thermal contributions to activation from the inner layer, the reason for their neglect (see Section II) was that the vibrational levels were far apart ($h\nu_1 \gg kT$), so that there would be discontinuity in the Tafel line.

However, this is at variance with knowledge of the energy levels associated with, for example, aq. H_3O^+ and, by implication, other solvated ions. According to Falk and Giguere²³, and Falk³⁴ for liquid H_2O , there is a continuum of energy states from 60 to 3444 cm^{-1} . Similar conclusions follow from O'Ferrall et al²².

Thus, classical (continuous) modes of heat transfer are available in water and, in particular, aq. H_3O^+ . The appreciable partial molar heat capacity (C_p) at room temperature for H_3O^+ , indicates a broad

range of frequencies giving classical C_p contributions and provides compelling evidence for the above conclusions.

By analogy to the gas phase, where translational energy is converted into vibrational energy (after collisions), it is reasonable to assume that the same process occurs in liquid water. The translational energy of free waters obeys a Boltzman distribution of energy and is in equilibrium with the H_3O^+ ion in solution. The vibrational energy levels of the H_3O^+ ion will also have a Boltzman distribution (at least up to a certain energy level). There will be sufficient activation of O-H bonds to sustain the reaction over the rates observed on various metals*.

The above arguments presuppose that H_3O^+ ion does not upset the equilibrium distribution among the levels by a permeation of the barrier to the electrode. This might be the case where the barrier thickness for proton transfer is assumed¹⁸ to be 0.5\AA . It is difficult to accept such a thickness, if one is to accept a model of hydrated ions in the double layer in which the double layer capacitance is independent

* For an electrochemical reaction:

$$\frac{i_o}{nF} = \frac{kT}{h} C_S e^{-\Delta H^*/RT} .$$

Taking $\Delta H^* = 15$ Kcal/mole and $i_o = 10^{-11}$ amp/cm², C_S comes out to be $\sim 10^{-3}$ molecules/cm². Thus, we need 10^{-3} molecules/cm² in the activated state for the reaction to go. Assuming a Boltzman distribution, the number of particles in high vibrational levels is given as:

$$N = N_o e^{-nh\nu/kT}$$

for $n = 1$, N comes out to be 10^4 molecules/cm², and for $n = 2$ the value comes out to be 10^{-2} molecules/cm². Thus, we have plenty of molecules in vibrational states to sustain the above rate.

N_o is taken to 10^{13} molecules/cm² as usual.

of ionic radius. On this basis, the minimum width of the barrier for proton transitions is $\sim 2.8\text{\AA}$.

A compelling piece of evidence that an oriented primary solvated ion solvent plays a role in the activation process for electron transfer reactions, comes from the study of hydrated electrons. The absorption spectrum of the hydrated electron shows a strong adsorption in the uv region, which is attributed to the 1s-2p transition. Jortner³⁶ calculated $h\nu_e$ using the Landau Hamiltonian (that used in the continuum electrostatic model), and Fueki et al³⁷ considered a layer of oriented water dipoles around the electron plus the Landau contribution. The results of these two calculations, as well as the experimental value, is summarized in Table 1.

This calculation does show that the inner sphere changes between the 1s and 2p states of the hydrated electron is large. There must, therefore, be some rearrangement of the inner sphere (thermal or electrostatic) before the electron transfer can occur.

TABLE I

| <u>Model</u> | $(\Delta H)_{\text{sol. calc.}}$ | $h\nu_{\text{calc}}$ | $(\Delta H)_{\text{sol. exp}}$ | $h\nu_{\text{exp}}$ |
|----------------|----------------------------------|----------------------|--------------------------------|---------------------|
| Continuum | 0.91 ev | 0.93 ev | 1.7 ev | 1.73 ev |
| Semi-Continuum | 1.95 ev | 1.86 ev | | |

Moreover, if the inner spheres of the reactant and product are different, there must be inner sphere activation to satisfy the Franck-Condon restriction of the electron transfer process⁹. Thus, the reactant and product activated state, must be in resonance and identical. If the inner sphere is different, activation must occur in it before the right

activated state can be obtained. The explicit omission of the inner sphere¹⁸ implies that the inner spheres for reactant and product are the same. Applied to $\text{H}_3\text{O}^+ + e^-(\text{M}) \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O}$, such a concept is unreasonable, and quantum mechanical treatment based on such a model is so far from reality that its consideration loses interest.

The applicability of employing the Born-Landau Hamiltonian for treatment of electrons in a polar medium is unlikely³⁶, apart from considerations made above. The Born-Landau Hamiltonian arises when the electronic adiabatic approximation is used to treat the problem of an electron trapped in a polar solvent. This approximation can be applied if the binding energy of the trapped electron is much smaller than the binding energy of the medium electrons. This is a reasonable approximation in a polar crystal where the electron binding energy is low. With polar liquids, the situation is different. The binding energies are higher, 1-2ev. This energy is comparable to the binding energy of the medium electrons (4-5 ev); the electronic adiabatic approximation is not valid. To calculate the binding energy of electrons in polar crystals, Jortner³⁶ suggests that the additional electron and the medium electron should be treated as an equal basis and uses the independent particle treatment better known as the self-consistent field scheme. The basic difference between these results and those obtained with the electronic adiabatic approximation is due to the fact that in the self-consistent field scheme the electronic polarisation does contribute to the binding energy of the electron. Thus, the potential then becomes of the form $\frac{e^2}{2r} \left(1 - \frac{1}{\epsilon_S} \right)$ instead of the $\frac{e^2}{2r} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_{\text{stat}}} \right)$ involved in the expression derived from the electronic adiabatic approximation. Thus, the

reorganisational energy would not be given by the Born-Landau equation. It would, correspondingly, not be given by the time-average Born energy, but by an equation for the change in the orientation energy on ejection of a charge in a polar dielectric.

2. The Quantum Mechanical Transition Probability

There are two ways whereby one can calculate the transition probability of electrons or protons between two states of equal energies⁴⁰. (a) from Perturbation theory; (b) from Tunneling theory. Most authors^{33,34} have treated the transition via tunneling theory. In respect to electrochemical kinetics, Christov⁶ and Bockris and Matthews⁸, following the work of Bell³⁸ and Johnston³⁹, have made numerical calculations of the transition probability using tunneling theory and barriers of various shape. Levich¹⁸ has criticized this approach, not only with respect to the electrochemical situation, but in all chemical reactions. The barrier created by solvent fluctuations is time-dependent. At time $t = 0$ the system is in its initial state and that part of the barrier connected with the presence of an adsorbed hydrogen does not exist. Similarly, at $t = t$ the system is in its final state, and the first part of the barrier does not exist. It is only the finite time interval (t) that the barrier forms and disappears as the transition occurs. The tunneling theory assumes that the barrier is fixed and independent of time and does not change during the course of transition. This latter approximation puts into doubt the use of the WKB approximation and the Gamow equation in calculating tunneling probability.

Consider the situation in Fig. 11. When we apply time-dependent perturbation theory, we assume initially the electron is in region (I) and after an interval of time, due to the action of a time-dependent perturbation (which results in the formation of the square barrier), the electron finds itself in region (III). There is no obvious way of introducing a small perturbation term in the Hamiltonian. However, for treating such problems, Bardeen⁴¹ has suggested a different approach. Instead of looking for exact solutions of an approximate Hamiltonian, we introduce approximate solutions of the exact Hamiltonian. Therefore, we select the following wave functions for the electron inside the barrier (Fig. 11).

$$\left. \begin{aligned} \Psi_i(x) &= a_{2i} e^{-k_2 x} & x \gg x_1 \\ \Psi_f(x) &= a_{2f} e^{+k_2 x} & x \ll x_2 \end{aligned} \right\} \quad (30)$$

Here, $\Psi_f(x)$ has to be matched to the correct solution for $x \gg x_2$, and will decay in the region $x \ll x_1$. On the other hand, $\Psi_i(x)$ has to be matched to the correct solution for $x \ll x_1$, and decay in the region $x \gg x_2$.

Initially, the electron is in the state represented by $\Psi_i(x)$ and we have to compute the transition probability for the electron to go into the state $\Psi_f(x)$. Let us form a time-dependent solution as a linear combination of $\Psi_i(x)$ and $\Psi_f(x)$ by the usual method. We write:

$$\Psi = C(t)\Psi_i(x)e^{-iE_i t} + d(t)\Psi_f(x)e^{-iE_f t} \quad (31)$$

Substitution of equation (31) in the time-dependent Schrodinger equation gives us finally⁴² the effective matrix element for tunneling as:

$$T_{if} = \int \Psi_f^* (H - E_i) \Psi_i dx . \quad (32)$$

This, after manipulation, can be expressed in the form:

$$|T_{if}|^2 = \frac{\hbar^4 \kappa_2^2}{m^2} |b_{2f}^*|^2 |a_{2i}|^2 . \quad (33)$$

In Fig. 11 the wave function in the regions I and III can be represented as:

$$\Psi_1 = a_{1i} e^{ik_1 x} + b_{1f} e^{-k_1 x}$$

$$\Psi_{III} = a_{3f} e^{ik_3 x} + b_{3f} e^{-ik_3 x} .$$

One can therefore obtain b_{2f} in terms of a_{3f} and a_{2i} in terms of a_{2i} by solving the standard matching problem⁴³ at x_1 and x_2 of Fig. 11. Introducing these results in equation (33), one obtains:

$$T_{if}^2 = \frac{\hbar^4 \kappa_2^2}{m^2} \cdot \frac{16k_1^2 k_3^2 |a_{1i}|^2 |a_{3f}|^2 e^{-2i\kappa_2 \omega}}{(k_1^2 + \kappa_2^2)(\kappa_3^2 + \kappa_2^2)} . \quad (34)$$

Using the Fermi golden rule of second-order perturbation theory, the transmitted current can be written as:

$$j_f = \frac{2\pi}{\hbar} |T_{if}|^2 \frac{dn}{dE_f} , \quad (35)$$

where $\frac{dn}{dE}$ is the density of states without spin in the transmitted wave and is given as⁴³:

$$|a_{3f}|^2 \frac{dn}{dE_f} = \frac{m}{2\pi \hbar^2 k_3} , \quad (36)$$

(where $|a_{3f}|$ is the coefficient of the wave function for the transmitted wave).

The incident current is:

$$j_i = \left(\frac{k_1}{h} \right) |a_{1i}|^2 . \quad (37)$$

Thus, the transmission coefficient is:

$$P_T = \frac{j_f}{j_i} = \frac{16k_1^2 k_2^2 k_3^2}{k_1 k_3 (k_1^2 + \kappa_2^2) (k_3^2 + \kappa_2^2)} e^{-2\kappa_2 \omega} \quad (38)$$

where $\omega = x_2 - x_1 =$ barrier thickness, and

$$\kappa_2 = \{2m(E_X - E_F)/h^2\}^{1/2} .$$

Equation (38) has the same form as Gamow's equation. We have, therefore, been able to prove that the time-dependent perturbation theory treatment of a square barrier penetration problem does give the same form of solution as the WKB approximation. (It would break down only in a non-adiabatic process).

Another argument which might invalidate the use of Gamow's equation, apart from that involving the change of the barrier during a transition, involves the fact that the top of the barrier fluctuates with time. Only if the tunneling time is less than the fluctuation time of the barrier, will the usual tunneling expression be valid. Consider the situation in Fig. 12. Due to the permeability of the barrier, there is a splitting in energy levels in the two wells. Let this splitting be δE . Let ψ_{II} and ψ_{IV} be the wave function in the wells II and IV. Then, we can say that, $\psi_{II} + \psi_{IV}$ has the energy $E_0 - \delta E$ and $\psi_{II} - \psi_{IV}$ has the energy $E_0 + \delta E$.

Hence, using the time-dependent Schrodinger equation, we can solve that find:

$$\Psi = \exp[-iE_0 t/h] \{ (\Psi_{II} + \Psi_{IV}) \exp[+i\delta E t/h] + (\Psi_{II} - \Psi_{IV}) \exp[-iEt/h] \}$$

or

$$\Psi = 2 \exp[-iE_0 t/h] \left\{ \cos \frac{\delta E t}{h} \Psi_{II} + i \sin \frac{\delta E t}{h} \Psi_{IV} \right\}. \quad (39)$$

We have chosen the phases such that the electron is in well (II) at $t = 0$. At $t = h\pi/\delta E$, the electron will be in well (IV). We define $t = h\pi/\delta E$ as the tunneling time. If $\delta E = 0.1$ ev, then $t = 10^{-14}$ sec.

If the fluctuation time of the barrier is more than the tunneling time, Gamow's equation is unaffected by this cause. For electron transfer reactions in aqueous solutions, the barrier is made up of vibrational or librational modes of the initial and final states. Since the vibrational and librational modes have a frequency about 10^{13} sec^{-1} and 10^{11} sec^{-1} respectively, the fluctuation time of the barrier should be greater than 10^{-13} . Thus, the tunneling time is smaller than the fluctuation time, for $\delta E = 0.1$ ev.

We have arbitrarily chosen the value of δE to be 0.1 ev. Physically, the value of δE is directly proportional to the interaction between the electron and the medium. From strong interaction, δE is generally of the order of $0.1 \sim 0.3 \text{ ev}^{44,45}$. In our situation, the interaction between the electron and the polar media is strong, an estimate of 0.1 ev for δE is reasonable.

Thus, the solution of the barrier leakage problem, using perturbation theory is the same as the one obtained by WKB approximation, and Gamow's equation should give an accurate estimate of the electron tunneling probability.

V. SUMMARY.

(1) Two models exist for activation in electrochemical reactions. In the first (thermal, T) there is considered to be an equilibrium of vibrational-rotational levels with the translational energy of the solvent. These levels are the main source of acceptor and donor states for electrons. The other model (the continuum electrostatic, E) discards the part played by such levels. Instead, the means of energy transfer from the solvent is a long-range electrostatic fluctuation which is to occur as a result of additivity of interaction between a large number of solvent molecules far from the ion.

(2) The rate-overpotential relation is deduced in a heuristic way on the basis of the two models. E does not predict a Tafel-like law.

(3) E neglects the electrostatic interaction between the librators in the inner solvent shell. However, the ground state of these molecules involved librations which would seem to give rise to electrostatically originated fluctuations in the ion's energy.

(4) The relation of k_{hom} and k_{het} does not diagnostically support E, as previously claimed.

(5) The calculated free energy of activation at E is not parallel to the experimentally observed one in respect to extensive solution data (52 systems).

(6) T does give a reasonable account of the current-potential relation, both in the constancy of β over 1 volt and its reduction towards zero at sufficiently large overpotentials.

(7) E does not reproduce the effect of change over solvent dielectric.

(8) The transfer of energy from the far out librators to the ion depends upon the applicability of polaron theory to solutions in water. However, the polaron theory loses its validity in structures in which there is no periodicity of the lattice.

(9) The assumption that there will be a large gap in energy between vibrational states in receptor ions, hence a discontinuous Tafel line, on model T, is not acceptable. In solution, there is a continuum of energy states in, for example, H_3O^+ over a large energy range. C_p for water is large at room temperatures: it shows the presence of classical modes.

(10) 1s-2p transitions in hydrated electrons cannot be rationalised unless the energy of nearest neighbour water molecules (i.e., not a continuum dielectric) is accounted for.

(11) The Born-Landau equation, - the basis of E-, is applicable to polar crystals, but unlikely to be valid for electric charge transfer in liquids.

(12) Time-dependent perturbation theory is consistent with the Gamow equation for time-dependent barriers concerned in charge-transfer.

(13) Electrostatic fluctuations contribute to the energy of ions undergoing transitions with electrons at interfaces. However, the origin of the energy of these fluctuations is in thermal equilibrium of the surrounding liquid into the nearest neighbour dipoles of the ions. Such an energy would add to the states in the electronic-vibrational and rotational levels of the ion, in addition to those which are present

due to equilibrium between solvent and ion.

(14) Finally, the essential situation is a distinction between a kinetics in which collisional activation is the model and statistical mechanics gives the distribution of energy and quantum mechanics the probability of transfer; versus a mode in which the reaction is supposed to occur because fluctuations in energy. It is noteworthy that a considerable theory of reactions in solution exist, in terms of encounters and statistical mechanics. Either an entirely incorrect type of approach has been taken to solution kinetics, or the continuum electrostatic (fluctuation) theory is invalid.

GLOSSARY OF SYMBOLS

e = Electronic charge

C_S = Surface concentration of reacting species

$n(\epsilon_f)$ = Fermi distribution

$\rho(\epsilon_f)$ = Density of states

$W_{if}(\epsilon_f)$ = Transition probability for the whole system

$\Delta\epsilon$ = Difference between the energy of the activated state and ground state

β = Transfer coefficient

$\Delta\phi$ = Potential difference across the electrode solution interface

l = length of barrier

m_e = mass of the electron'

$E_X = E_F$ = barrier height

η = overpotential

E_{act} = activation energy

κ = transmission coefficient

k_{hom} = homogeneous rate constant

k_{het} = heterogeneous rate constant

Z_{hom} = Collision number for homogeneous reactions

Z_{het} = Collision number for heterogeneous reactions

J_{fn} = Energy of the final state

J_{in} = Energy of the initial state

r_1 = radius of ion 1

r_2 = radius of ion 2

r = distance of closest approach

ϵ_{opt} = optical dielectric constant

ϵ_{stat} = static dielectric constant

D_{AB} = diffusion coefficient

r_{AB} = nearest neighbour dipole

a = Morse constant

x_0 = Equilibrium separation between the two Morse curves

$\langle \Delta H_i^{0*} \rangle$ = activation energy for the cathodic reaction

D_1 = dissociation energy

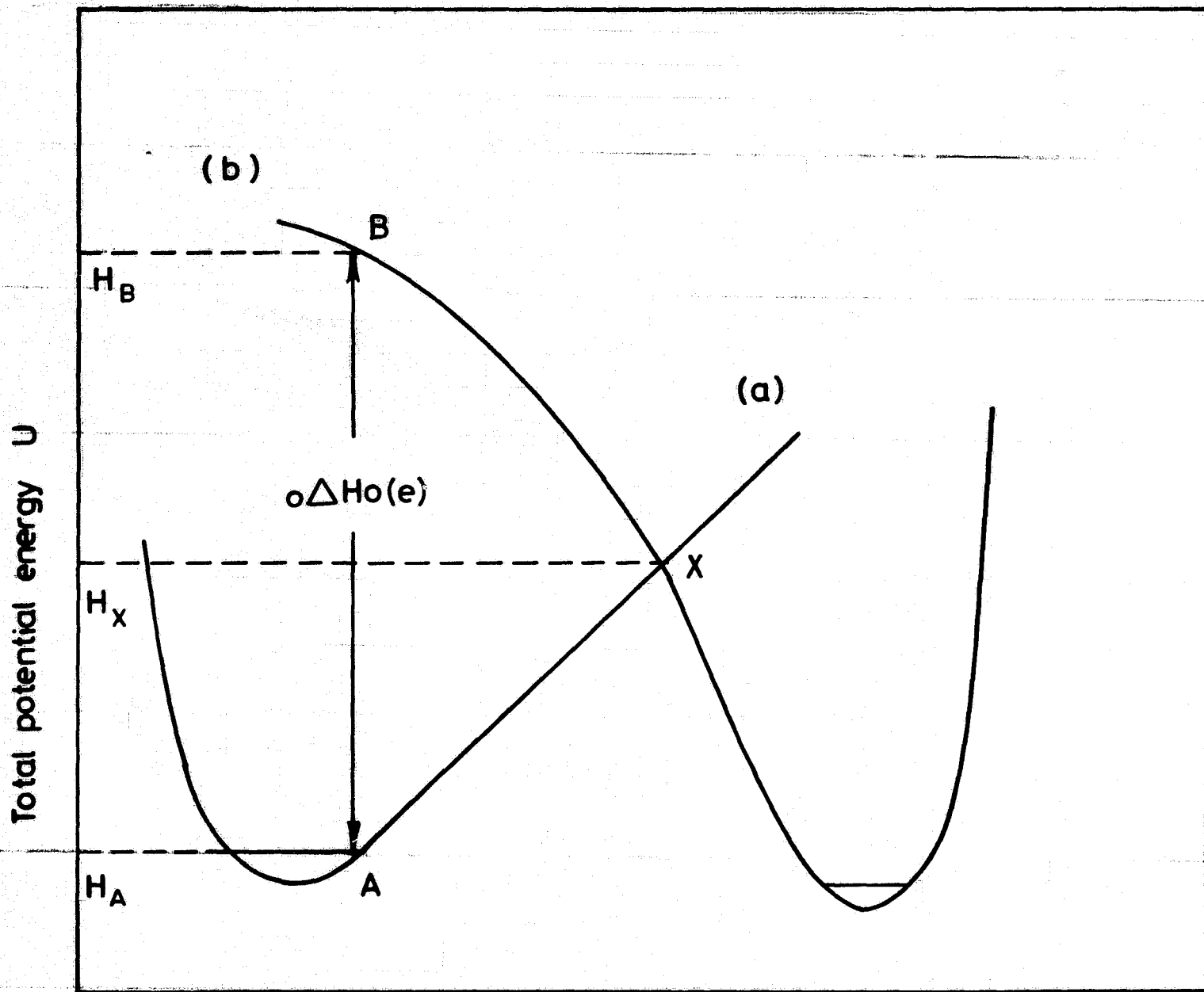
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Proton coordinated.

Figure 1.

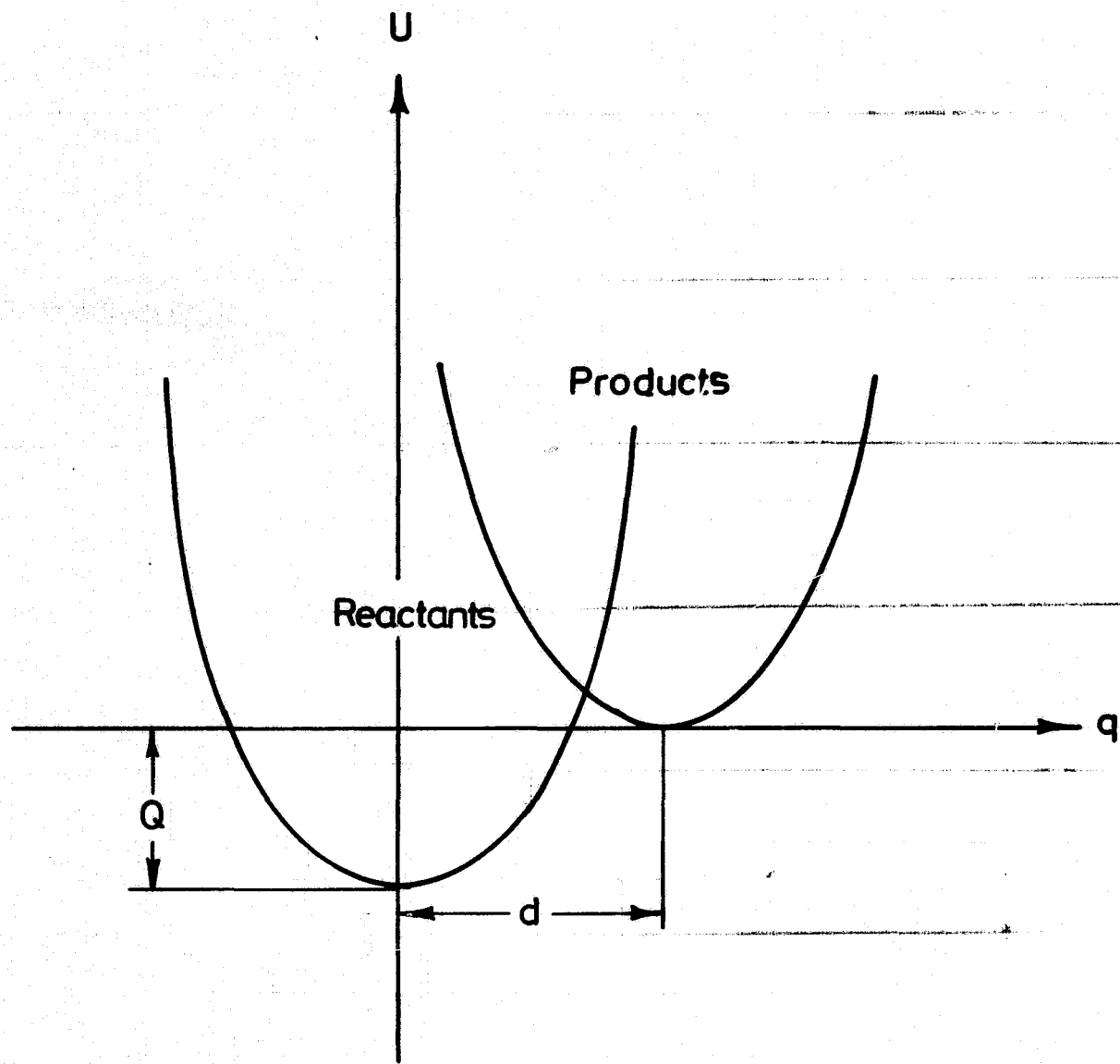


Figure 2.

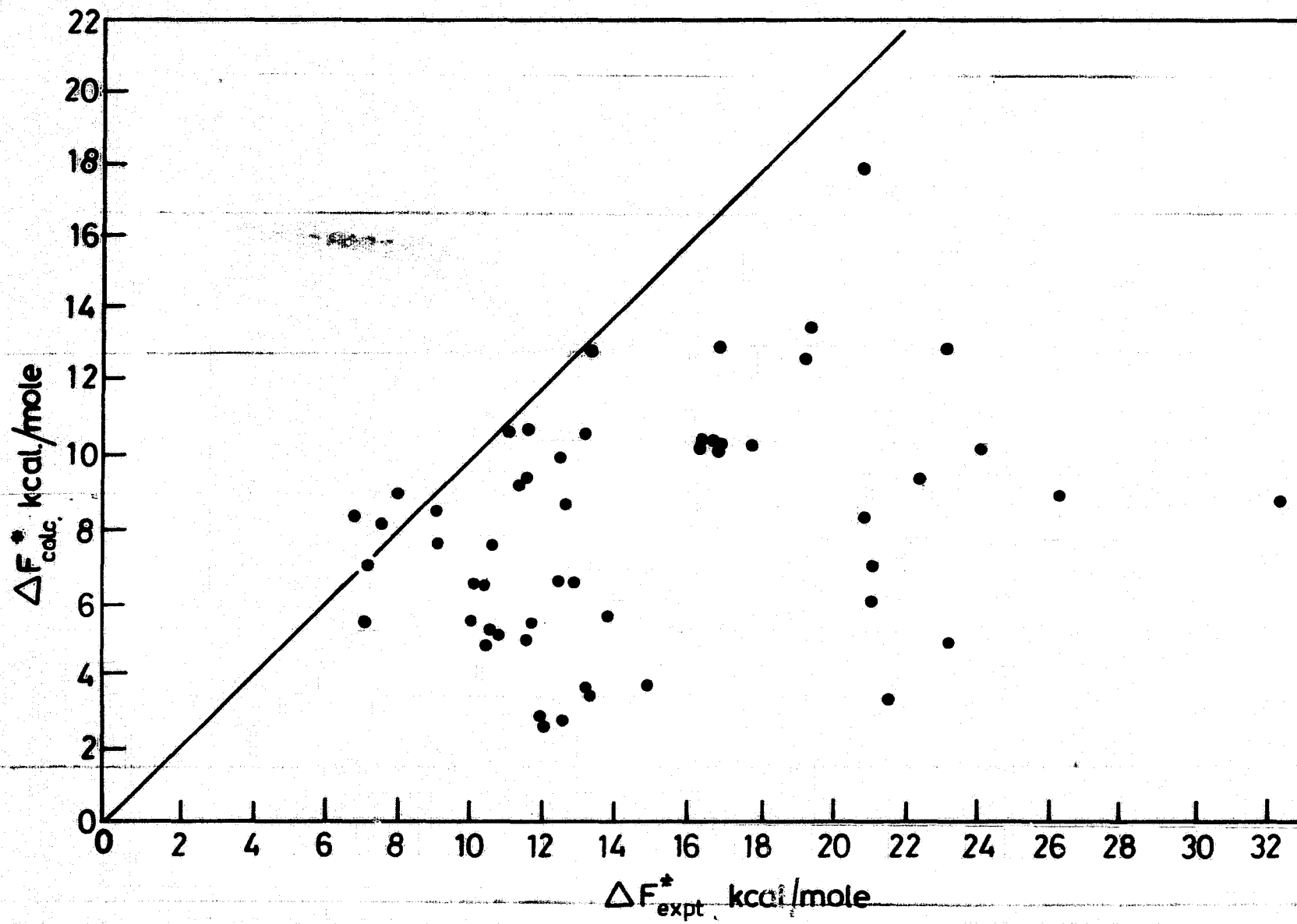


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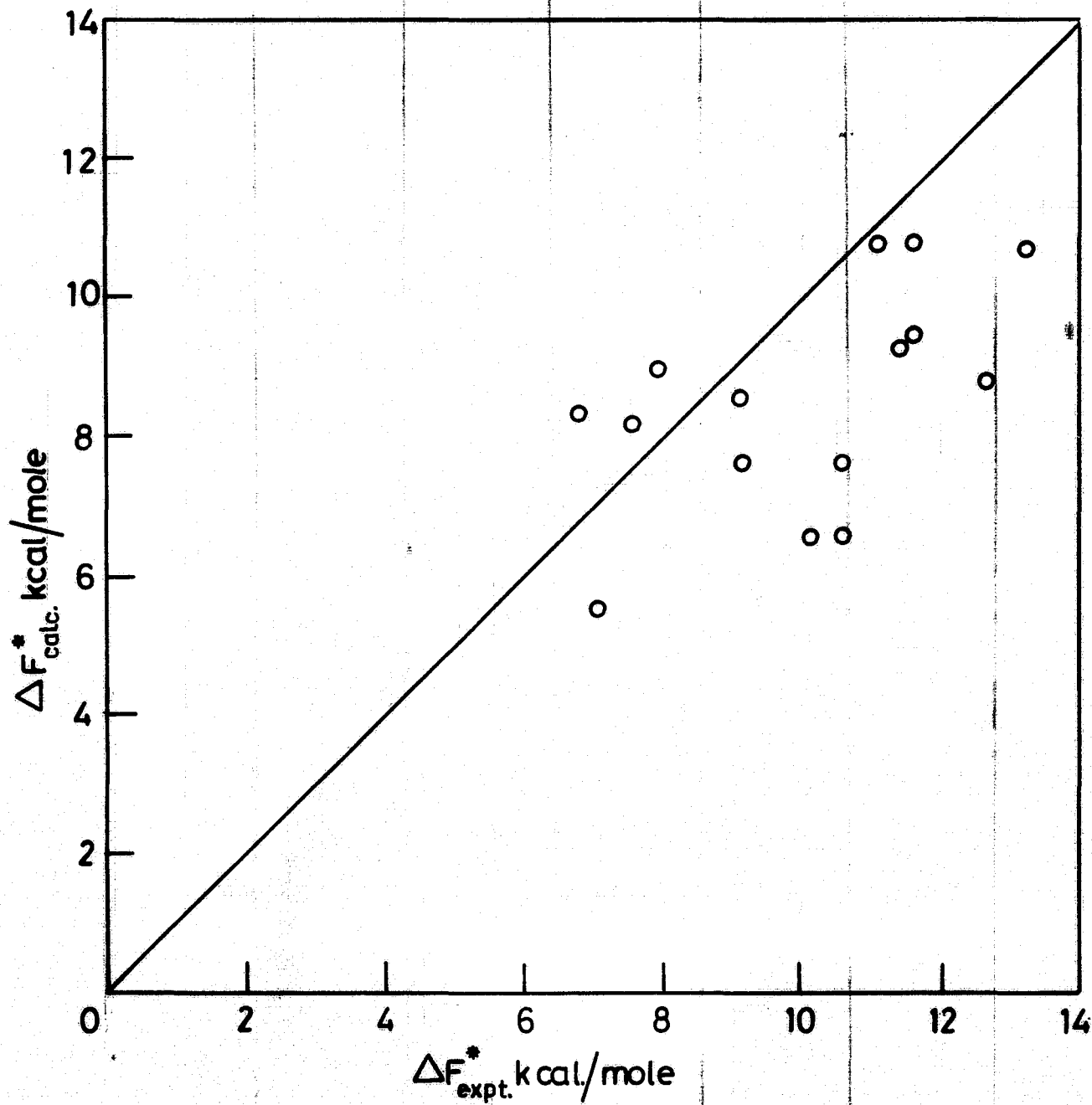


Figure 4(a).

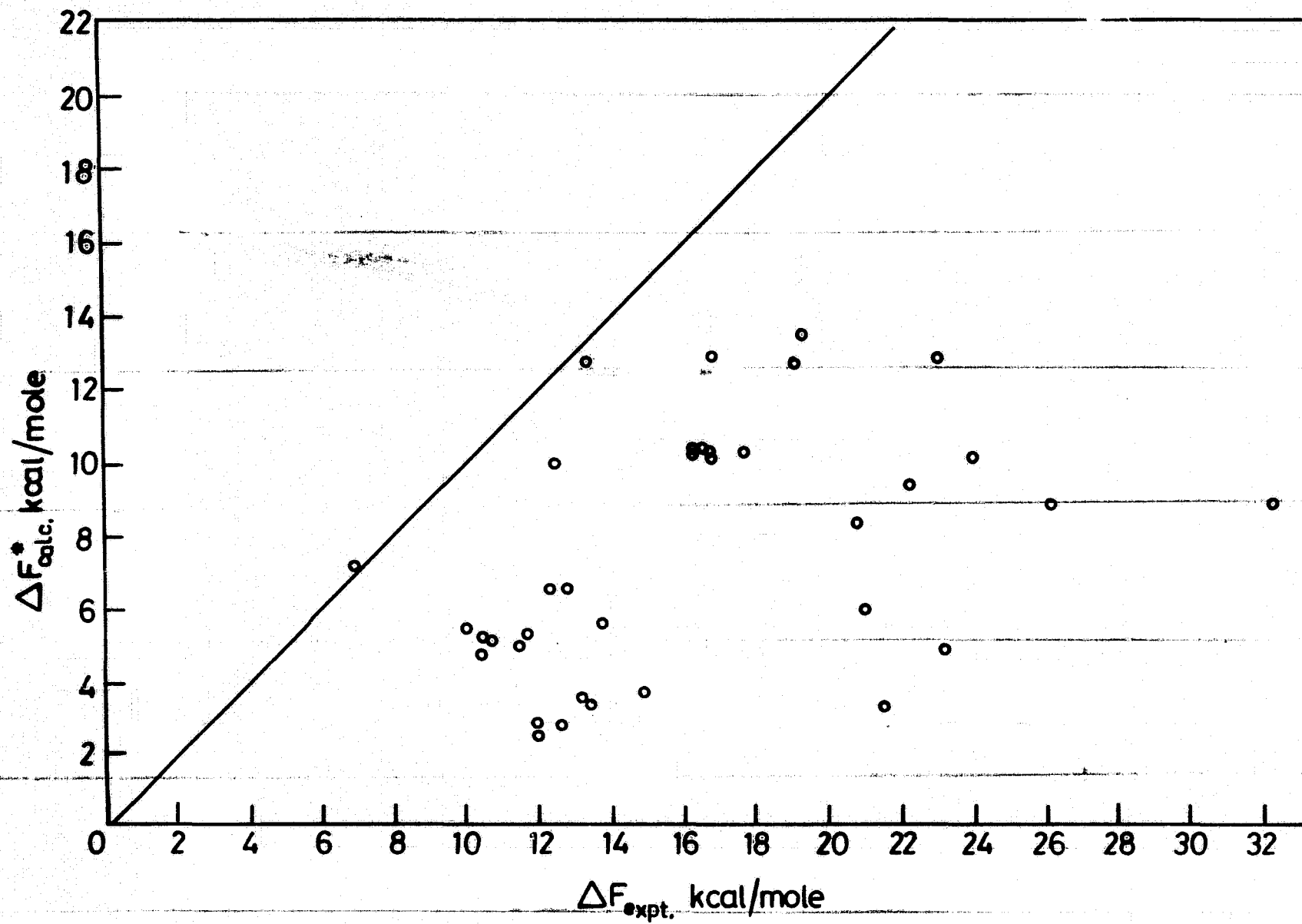


Figure 4(b)

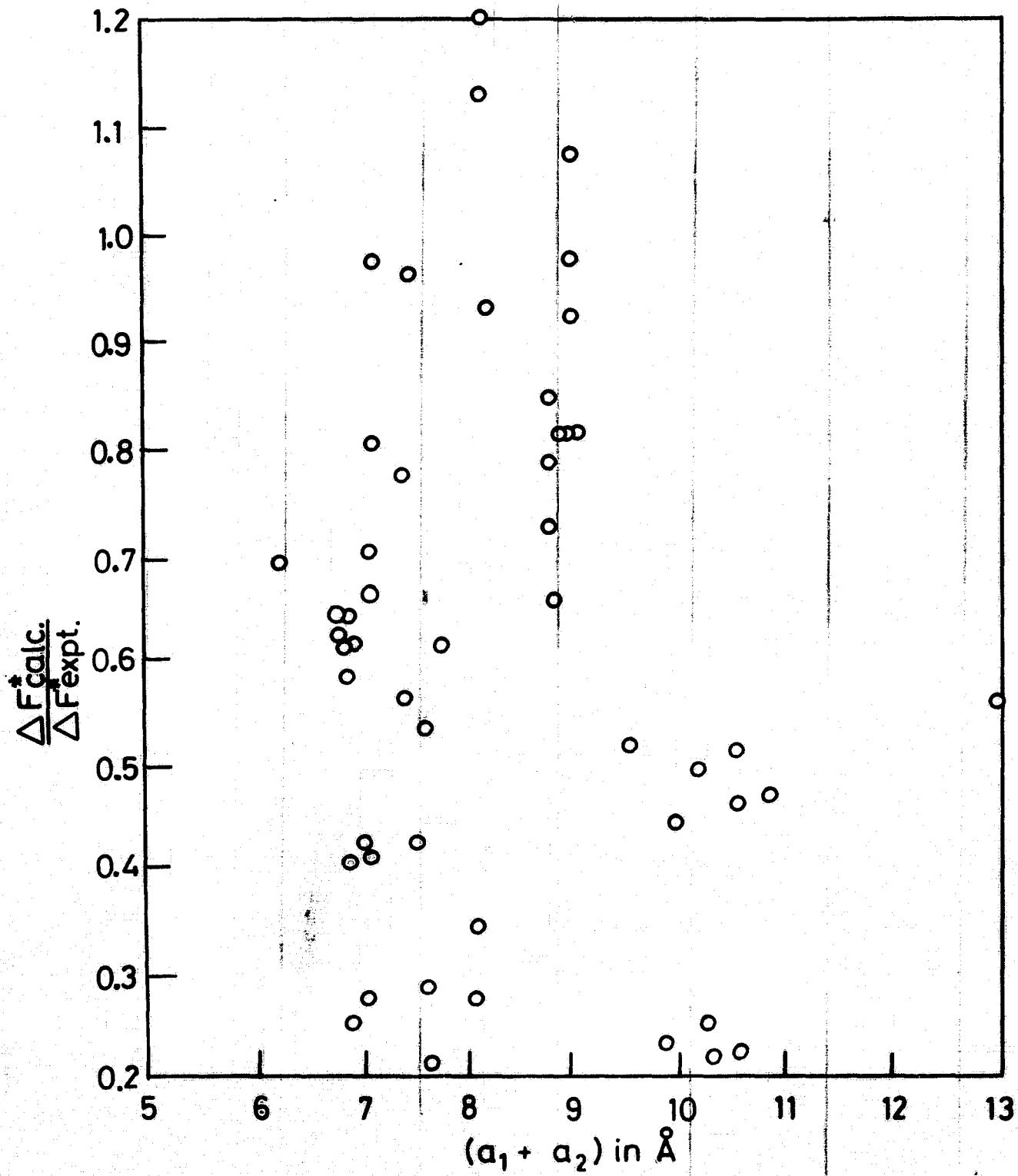


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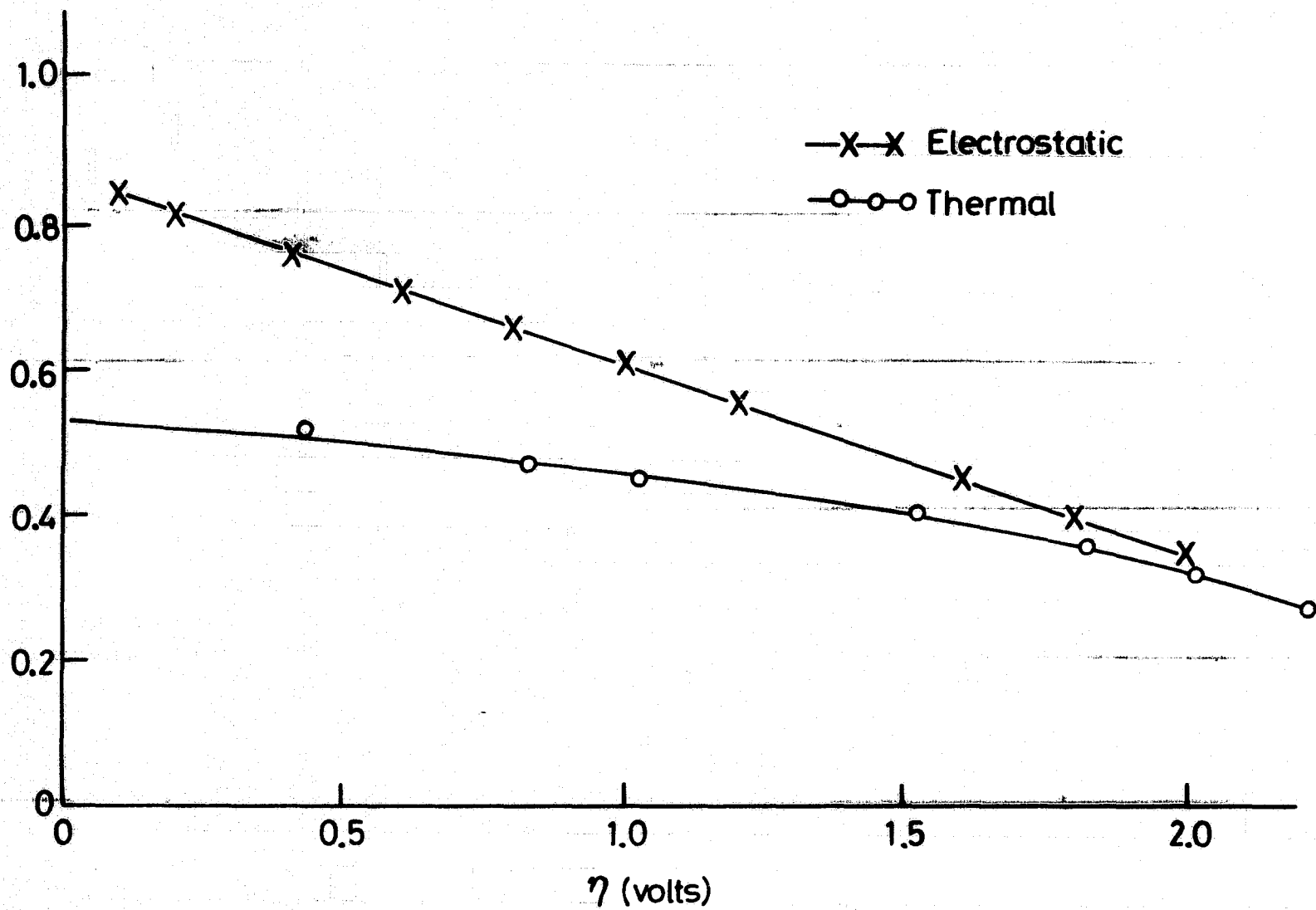


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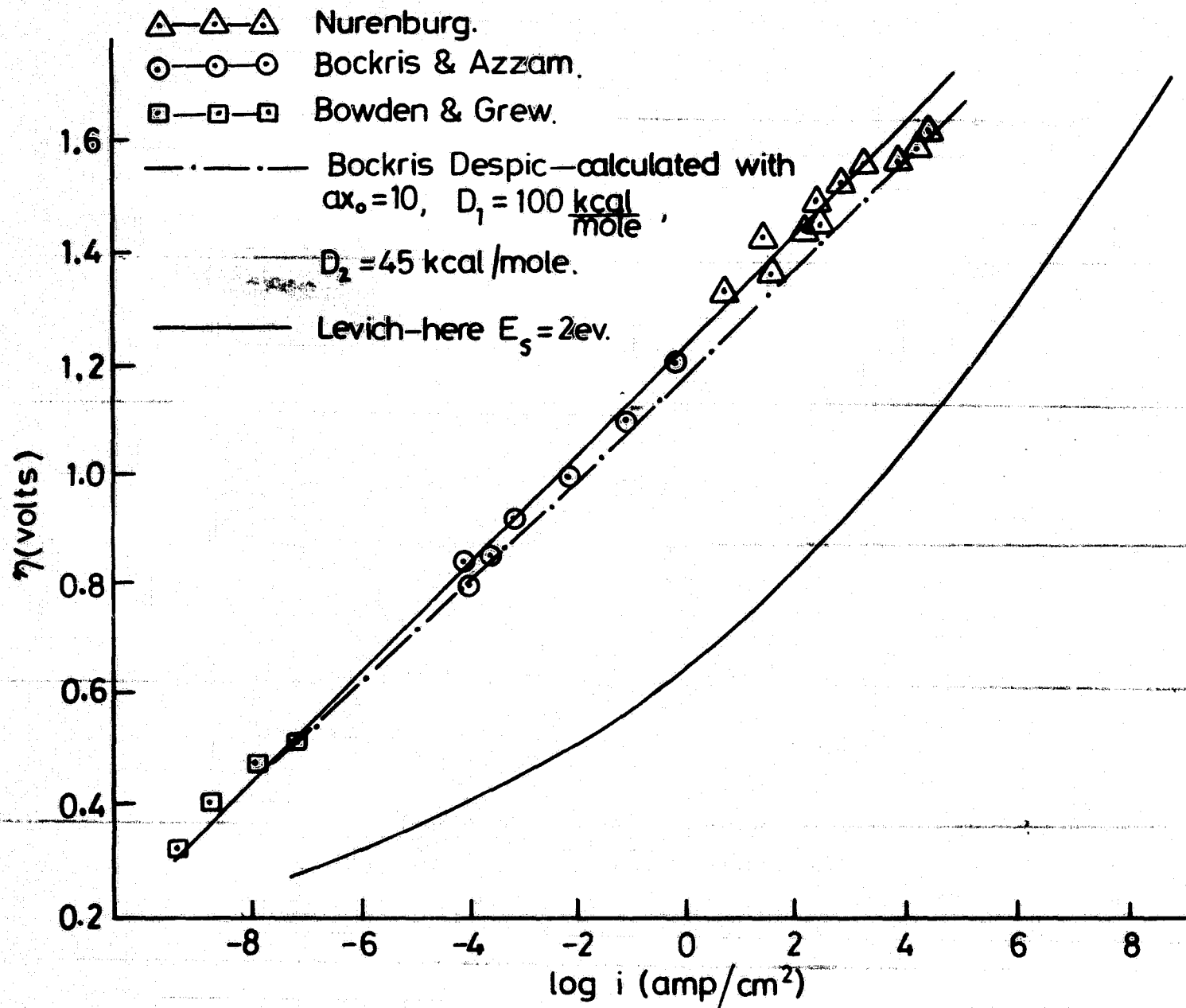
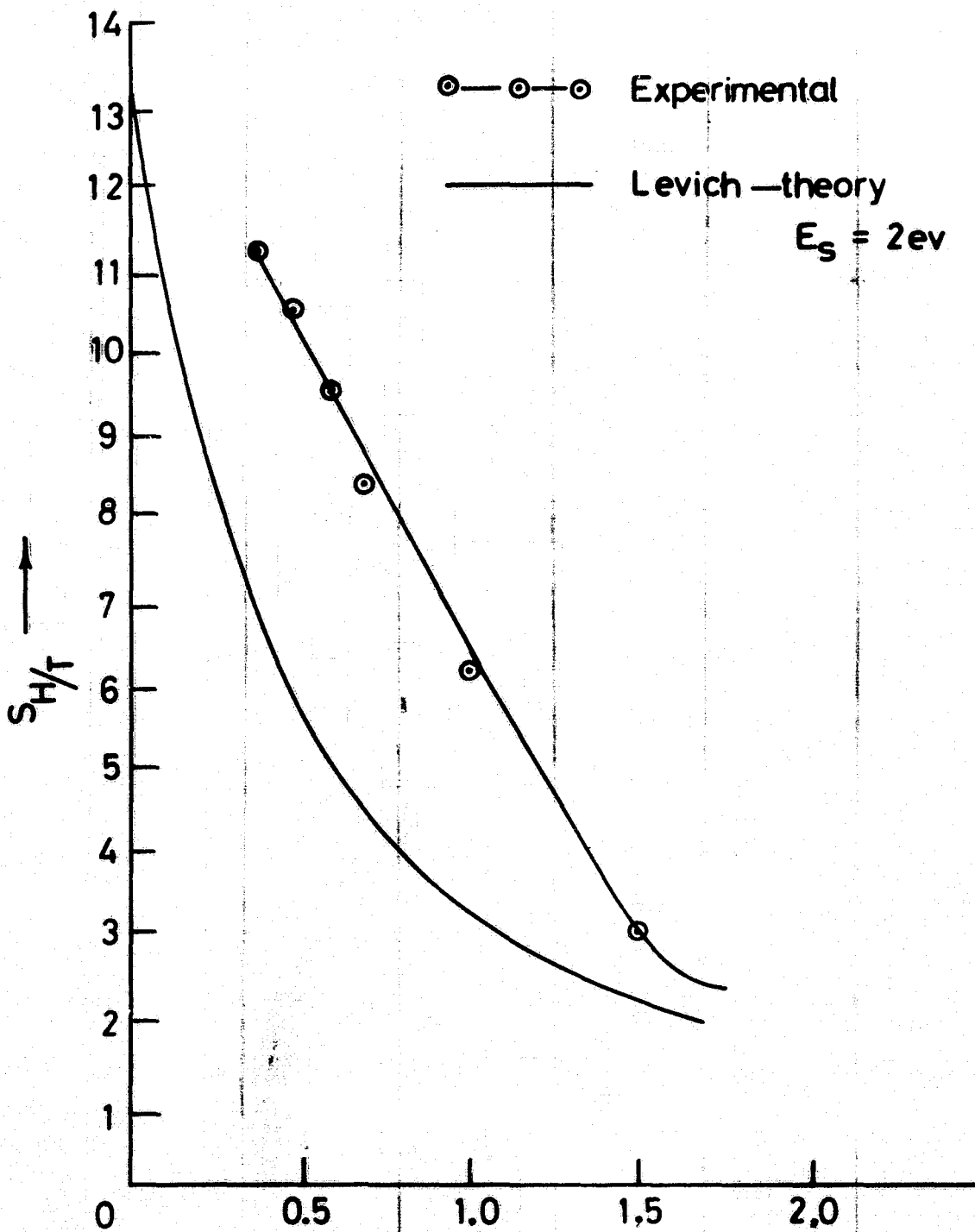


Figure 7



η in volts
Figure 8(a)

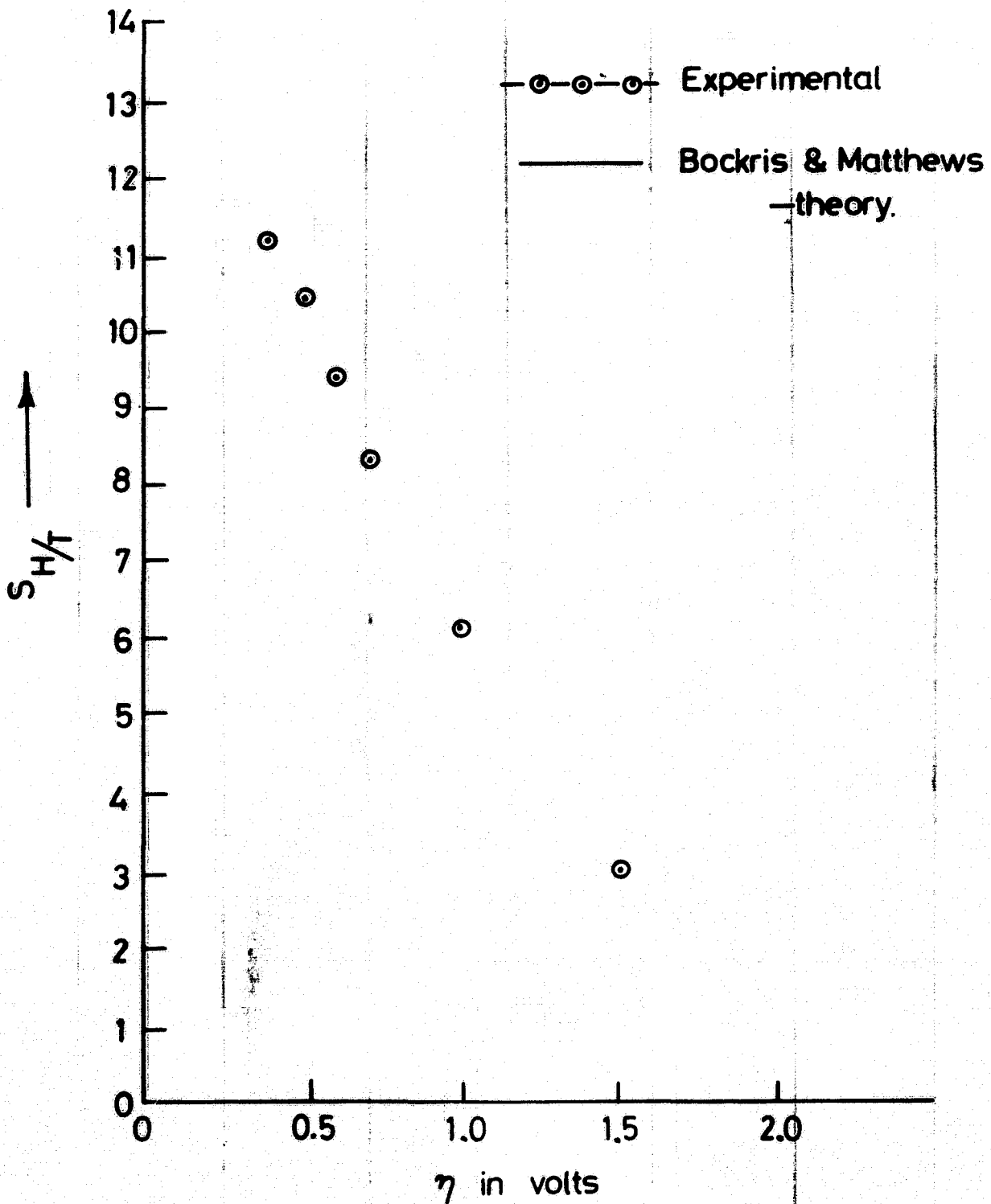


Figure 8(b)

ELECTROSTATIC

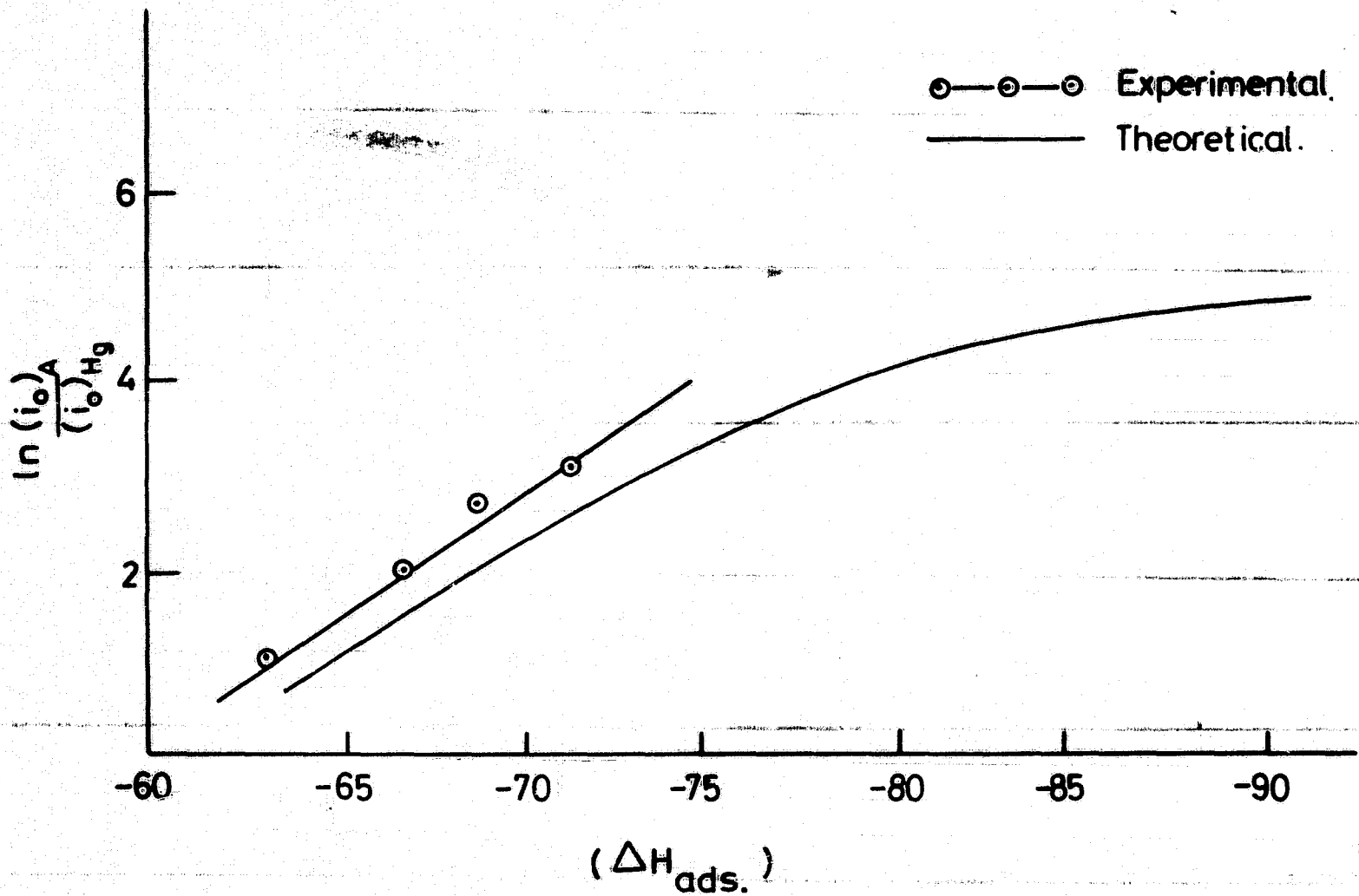


Figure 9(a)

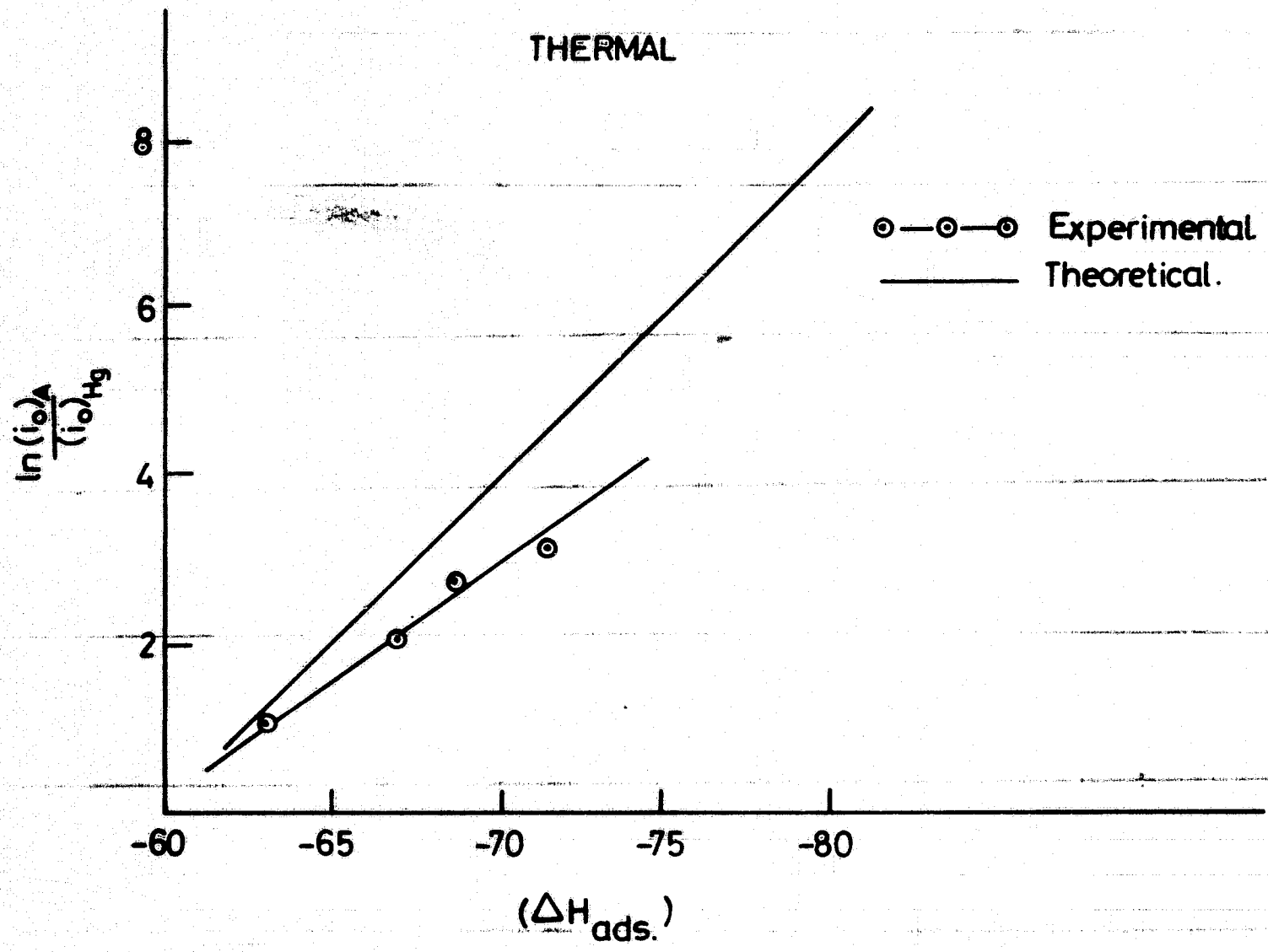


Figure 9(b).

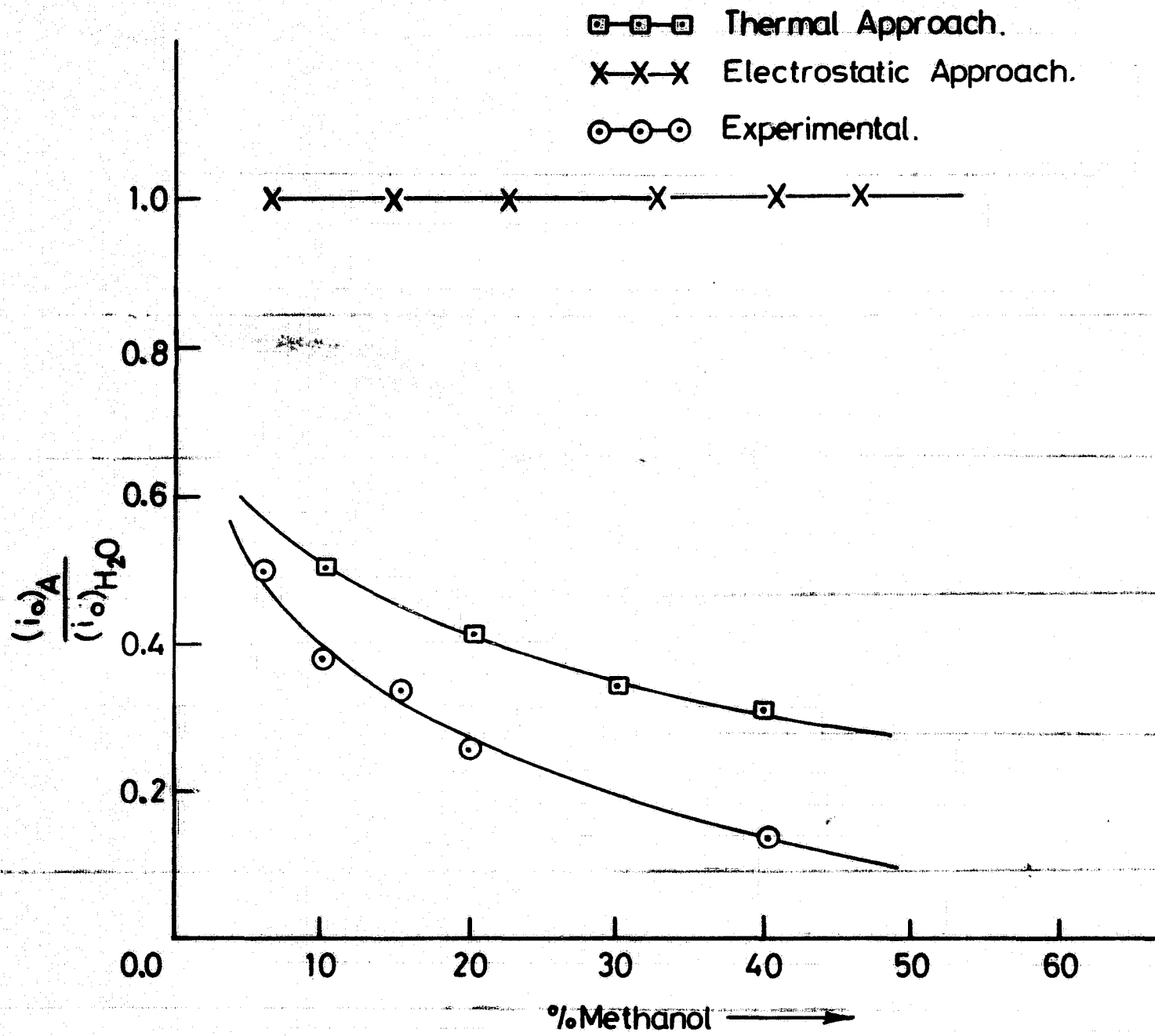


Figure 10.

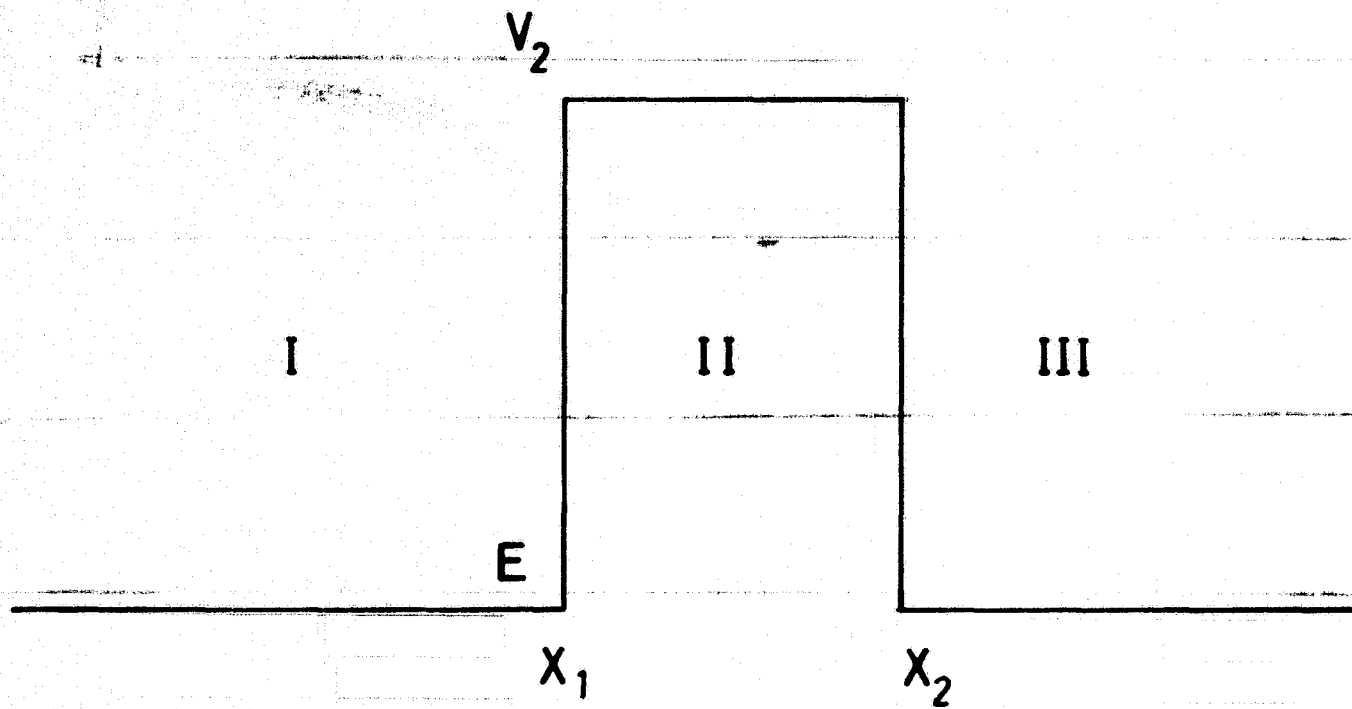


Figure 11

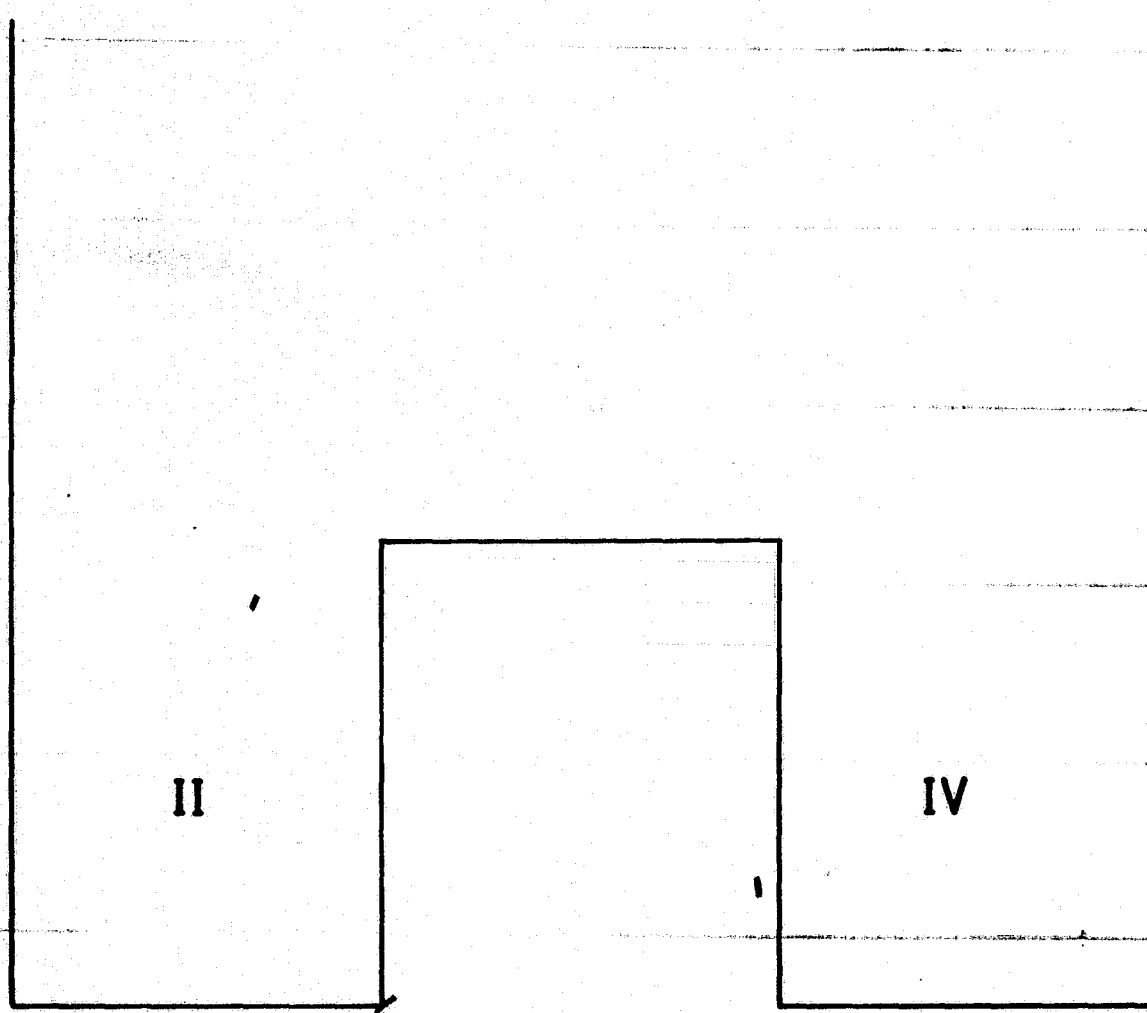


Figure 12.

ANNOTATIONS FOR FIGURES

- Figure 1. Potential energy-distance profile for h.e.r.: H_A is the ground state energy level of the reactants; curves (a) and (b) show the variation of potential energy with internuclear separation for $M(e^-) \dots H^+-OH_2$ and $M-H\dots OH_2$, respectively; ${}_o\Delta H_{o(e)}$ is the standard enthalpy of reaction for reactants in their ground state.
- Figure 2. Potential energy-distance profile using harmonic oscillators.
- Figure 3. Plot of ΔF^*_{calc} (from electrostatic approach) against ΔF^*_{expt} for electron transfer reactions.
- Figure 4. (a) Plot of ΔF^*_{calc} (from electrostatic approach) against ΔF^*_{expt} for reactants with ligands other than water or ammonia.
- (b) Plot of ΔF^*_{calc} (from electrostatic approach) against ΔF^*_{expt} for reactants involving water and ammonia ligands.
- Figure 5. Plot of $\frac{\Delta F^*_{calc}}{\Delta F^*_{expt}}$ against the distance of closest approach for the two reactions.
- Figure 6. Variation of transfer-coefficient with potential.
- Figure 7. Tafel lines from thermal and electrostatic approaches compared with experiment.

Figure 8. (a) Variation of the separation factor with potential-electrostatic approach.

(b) Variation of the separation factor with potential-thermal approach.

Figure 9. (a) Variation of $\ln \frac{(i_o)_A}{(i_o)_{H_g}}$ with the heat of adsorption in the electrostatic approach.

(b) Variation of $\ln \frac{(i_o)_A}{(i_o)_{H_g}}$ with heat of adsorption for thermal approach.

Figure 10. Variation of $\ln \frac{(i_o)_A}{(i_o)_{H_2O}}$ with the variation of methanol concentration.

Figure 11. Tunneling through a square barrier.

Figure 12. Double well problem.

ON THE THEORY OF TUNNELLING IN ELECTRON AND
PROTON TRANSFER REACTIONS

ON THE THEORY OF TUNNELLING IN ELECTRON AND
PROTON TRANSFER REACTIONS

Abstract

The concept of tunnelling in the theory of electron and proton transfer reactions has recently been questioned on the ground that the situation is a non-stationary one. It has been suggested that time-dependent perturbation theory should be applied to obtain the quantum mechanical transition probability. We have done this for a square barrier. The result for most reactions is the same as obtained by the WKB approximation.

1. INTRODUCTION

A large amount of work present in the literature (1) concerning theories of electron or proton transfer reactions in solution, either at an electrode or in the bulk of the solution, uses the concept of electron and proton tunnelling through a barrier. For electron transfer reactions at an electrode-solution interface, the theory has been developed extensively by Gurney (2), Gerischer (3), and Bockris and Matthews (4). These authors also consider proton tunnelling at the electrode-solution interface. Marcus et al (5) have used the same concepts for electron transfer reactions in the bulk of the solution. Bell (6), Johnston (7) and Caldin and Kasparian (8) have considered proton tunnelling in the theory of proton transfer reaction in the bulk of the solution. However, recently (9, 10), the tunnelling approach has been criticized on the ground that the process of both electron and proton transfer at an interface is of a non-stationary nature. It is contended that the use of Gamow's

equation is then erroneous: time-dependent perturbation theory must be used. We have calculated the transmission probability of a plane wave going through a square barrier which is caused to change by the transition, using time-dependent perturbation theory.

Another aspect of the same problem involves the fact that the barrier itself may fluctuate with time, independently of the act of transfer, which causes it locally to decompose. Then, also, Gamow's equation may be invalid. We have also examined this problem.

2. CALCULATION

2.1 The WKB method

Consider a square barrier as shown in Fig. 1. In the three regions the wavefunctions may be represented as:

$$\begin{aligned}\psi_I &= a_{1i} \exp(ik_1x) + b_{1f} \exp(-ik_1x), \\ \psi_{II} &= a_{2i} \exp(-\kappa_2x) + b_{2f} \exp(\kappa_2x), \\ \psi_{III} &= a_{3i} \exp(ik_3x) + b_{3f} \exp(-ik_3x).\end{aligned}\tag{1}$$

The well-known solution of the tunnelling problem (11), using the WKB approximation, gives the transition probability, P_T , as

$$P_T = \frac{j_3}{j_1} = \frac{16k_1^2\kappa_2^2}{(k_1^2 + \kappa_2^2)(k_3^2 + \kappa_2^2)} \exp(-2\kappa_2\omega),\tag{2}$$

where $\omega = (x_2 - x_1)$ is the barrier thickness, and $\kappa_2 = \{2m(V_2 - E)/\hbar^2\}^{1/2}$.

2.2 Time-dependent perturbation theory approach

Since P_T is small, a perturbation theory approach seems admissible. However, it is not clear that one may introduce a term in the Hamiltonian which is small. Bardeen (12) has suggested that, for solving problems of this type, instead of introducing states which are the exact solution of an approximate Hamiltonian, we should introduce approximate solutions of the exact Hamiltonian. We therefore choose the following wavefunctions for the electron inside the barrier (fig. 1).

$$\psi_i(x) = a_{2i} \exp(-\kappa_2 x), \quad x \leq x_1$$

and

$$\psi_f(x) = a_{2f} \exp(\kappa_2 x), \quad x \geq x_2$$

Hence, $\psi_f(x)$ has to be matched to the correct solution for $x \geq x_2$, and will decay in the region $x \leq x_1$. On the other hand, $\psi_i(x)$ has to be matched to the correct solution for $x \leq x_1$, and decay in the region $x \geq x_2$.

Initially, the electron is in the state represented by $\psi_i(x)$ and we have to compute the transition probability for the electron to go into the state $\psi_f(x)$. Let us, therefore, express the total wavefunction as a linear combination of $\psi_i(x)$ and $\psi_f(x)$. We write:

$$\psi_{II} = C(t)\psi_i(x)\exp(-iE_i t) + d(t)\psi_f(x)\exp(-iE_f t). \quad (4)$$

Substitution of eq. (4) into the time-dependent Schrodinger equation gives us:

$$\begin{aligned} & C \exp(-iE_i t)H\psi_i + d \exp(-iE_i t)H\psi_f \\ &= iC\psi_i \exp(-iE_i t) + C\psi_i E_i \exp(-iE_i t) \\ &+ id\psi_i \exp(-E_f t) + d\psi_f E_f \exp(-iE_f t). \end{aligned} \quad (5)$$

Now, initially, the electron is in $\psi_i(x)$. Hence, we can set $C = 1$, $d = 0$ and $C = 0$. (That $C = 0$ follows from the normalization condition that $d(CC^* + dd^*)/dt = 0$). Therefore, (5) gives:

$$id\psi_f \exp(-iE_f t) = (H - E_i)\psi_i \exp(-iE_i t),$$

or

$$id = \exp[i(E_f - E_i)t] \int \psi_f^*(H - E_i)\psi_i dx. \quad (6)$$

Let us, therefore, define the effective matrix element for tunnelling to be*:

$$T_{if} = \int \psi_f^*(H - E_i)\psi_i dx. \quad (7)$$

We can express the integral in a more symmetric form by subtracting $\psi_i(H - E_f)\psi_f^*$, since this term gives no contribution for the range of integration $x \geq x_1$.

Therefore, we may rewrite eq. (7) as:

$$T_{if} = \int_{x_B}^{\infty} [\psi_f^*(H - E_i)\psi_i - \psi_i(H - E_f)\psi_f^*] dx, \quad (8)$$

$$x_i \leq x_B \leq x_2.$$

Integrating eq. (8) by parts gives us:

$$T_{if} = \frac{\hbar^2}{2m} \left(\psi_f^* \frac{d\psi_i}{dx} - \psi_i \frac{d\psi_f^*}{dx} \right)_{x_B} = -ihj_{if}, \quad (9)$$

where j_{if} is the current operator. Using eq. (3) in eq. (9) yields:

* This can only be done if the barrier changes slowly with time, for example, see Schiff (13).

$$T_{if} = (h^2 \kappa_2 / m) b_{2f}^* a_{2i}. \quad (10)$$

One now obtains b_{2f} in terms of a_{3f} , and a_{2i} in terms of a_{1i} by solving the standard matching problem (13) at x_1 and x_2 of fig. 1; one then introduces them into eq. (10), and obtains:

$$|T_{if}|^2 = \frac{h^4 \kappa_2^2}{m^2} \frac{16k_1^2 k_3^2 |a_{1i}|^2 |a_{3f}|^2}{(k_1 + \kappa_2)(k_3 + \kappa_2)} \exp(-2\kappa_2 \omega), \quad (11)$$

where the terms are as defined in eq. (1). Using the Fermi golden rule of second order perturbation theory, the transmitted current can now be written as:

$$j_f = h^{-1} |T_{if}|^2 dn/dE_f, \quad (12)$$

where dn/dE_f is the density of states without spin in the transmitted wave and is given as (13):

$$dn/dE_f = |a_{3f}|^{-2} m/2\pi h^2 k_3. \quad (13)$$

The incident current can be written as:

$$j_i = (hk_1/m) |a_{1i}|^2. \quad (14)$$

Thus, the transmission coefficient is:

$$P_T = \frac{j_f}{j_i} = \frac{16k_1^2 \kappa_2^2 k_3^2}{k_1 k_3 (k_1 + \kappa_2)(k_3 + \kappa_2)} \exp(-2\kappa_2 \omega), \quad (15)$$

using for j_f the expression resulting from the substitution of eqs. (11) and (13) in eq. (12). Comparing eq. (15) with eq. (2), one finds that the exponential part is the same, but there is a difference in the pre-

exponential part. The ratio of the expressions for P_T given in (2) and (15) is k_3^2/k_1k_3 . Since both k_1 and k_3 have the same order of magnitude, the factor will in general be unity.

Thus, the transmission probability of an electron penetrating a square barrier using time-dependent perturbation theory is the same as that obtained from the WKB approximation.

3. EFFECT OF FLUCTUATIONS OF THE BARRIER ON LEAKAGE THROUGH THE BARRIER

An argument which might invalidate the use of Gamow's equation both for electron and proton tunnelling, apart from that involving the change of the barrier during a transition, involves the fact that the barrier may fluctuate with time. If the tunnelling time is more than the fluctuation time of the barrier, the usual tunnelling expression will indeed be valid. To investigate this aspect, consider the situation in fig. 2. Due to the permeability of the barrier, there is a splitting of the energy levels in the two wells. Let this splitting be δE . Let ψ_{II} and ψ_{IV} be the wavefunctions in the wells II and IV. Then, we can say that $\psi_{II} + \psi_{IV}$ has the energy $E_0 - \delta E$ and $\psi_{II} - \psi_{IV}$ has the energy $E_0 + \delta E$.

Hence, using the time-dependent Schrodinger equation, we can solve to find:

$$\psi = \exp[-iE_0 t/h] (\psi_{II} + \psi_{IV}) \exp[+i\delta Et/h] + (\psi_{II} - \psi_{IV}) \exp[-iEt/h] ,$$

or

$$\psi = 2\exp[-iE_0 t/h] \{ \cos(\delta Et/h) \psi_{II} + i \sin(\delta Et/h) \psi_{IV} \} . \quad (16)$$

We have chosen the phases such that the particle is in well II at $t = 0$. It is interesting to note that at $t = h\pi/\delta E$, the electron will be in well IV. We can hence define $t = \frac{1}{2}h\pi/\delta E$ as the tunnelling time. As we have mentioned before, the tunnelling time t has to be small compared to the fluctuation time of the barrier for Gamow's equation to be applicable. For electron and proton transfer reactions in aqueous solutions, the barrier is made up of vibrational or librational modes of the initial and final states. These modes have a frequency of about 10^{13} sec^{-1} for water. Thus the fluctuation time of the barrier for water should be greater than or equal to 10^{-13} sec . Let us therefore evaluate the tunnelling time. The main problem in this calculation is the estimation of δE , the splitting energy. We will use the technique developed by Denison and Uhlenbeck (14) for this purpose. These authors found that for a double well potential of the form shown in Fig. 2, the splitting energy is given as:

$$\delta E = \frac{h[2m(E - V)]^{1/2}}{2\pi m l [\exp\{(2\pi l/h)[2m(E - V)]^{1/2}\}]^2}, \quad (17)$$

where $(E - V)$ is the barrier height, m the mass of the tunnelling particle and l the barrier thickness. Let us now evaluate the magnitude of δE and the tunnelling time for various electron and proton transfer reactions and see when Gamow's equation is affected by the fluctuating character of the barrier.

3.1 Electron tunnelling

The barrier parameters for electron tunnelling in the hydrogen evolution reaction has been estimated for electron transfer from mercury

to protons in solution by Matthews (15) to be 70kcal/mole for $(E - V)$ and $l = 2.4 \times 10^{-8}$ cm. Thus, δE from eq. (17) comes out to be 0.15 eV and hence

$$t = (h/2E)10^{-14} \text{ sec,}$$

which is significantly smaller than the fluctuation time of the barrier ($\approx 10^{-13}$ sec). Consequently, the use of Gamow's equation is unaffected by fluctuations of the barrier.

3.2 Proton transfer

3.2.1 Bulk proton transfer

Several proton transfer reactions were considered and their δE and the tunnelling time calculated. The results are summarized in table 1. The values of $(E - V)$ and l are taken from ref. (8). In five out of the six cases, the equation is applicable.

3.2.2 Electrochemical proton transfer

From the ground vibrational level of H_3O^+ ion, the height of the barrier for proton transfer in the electrochemical hydrogen evolution reaction has been estimated by Matthews (15) to be 20 kcal/mole and the width to be 2.42 \AA . However, tunnelling does not occur from the ground state of H_3O^+ . The first vibrational level of H_3O^+ is 10kcal/mole and the width is 2 \AA . The splitting energy for that case using eq. (17) is 0.07 eV, and hence the tunnelling time is approximately 1.3×10^{-14} sec, smaller than the fluctuation time for the barrier. Consequently, Gamow's equation is applicable.

4. CONCLUSIONS

In this article we have shown that:

(i) in respect to the fundamental time-dependence of a barrier in a chemical process, the solution for the transmission probability according to time-dependent perturbation theory is the same as that from the WKB approximation;

(ii) in respect to the fluctuating effects of the surrounding solvent on the barrier, the WKB approximation is applicable in nearly all the examined proton and electron tunnelling cases.

TABLE I

DATA RELEVANT TO CALCULATION OF THE SPLITTING ENERGY IN
PROTON TRANSFER

| Reaction (ref.) | (E-V) (kcal/mole) | I (A) | δE (eV) | tunnelling time (sec) | Comments about WKB approximation |
|---|----------------------|----------|--------------------|--------------------------|-------------------------------------|
| 1. $\text{CH}_2\text{BrC}\cdot\text{MePh}\cdot\text{H}+\text{OEt}^-$ | 22.1 | 1.59 | 0.06 | 1.6×10^{-14} | valid |
| 2. $\text{RH} + \text{D}_2\text{O}$ a) | 13.1 | 1.26 | 0.08 | 1.3×10^{-14} | valid |
| 3. $\text{RH} + \text{F}^-$ a) | 18.0 | 1.17 | 0.09 | 1.2×10^{-14} | valid |
| 4. $\text{RH} + \text{F}^-$ a) ($\text{H}_2\text{O} + \text{NaBr}(5\text{M})$) | 24.2 | 1.46 | 0.01 | 1.1×10^{-13} | doubtful |
| 5. $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{CH}_2^- + \text{HOAc}$ | 10.1 | 1.66 | 0.06 | 1.6×10^{-14} | valid |
| 6. $\text{H}_3\text{O}^+ + \text{H}_2\text{O}$ | | | 0.12^{b} | 8.47×10^{-15} | valid |

a) $\text{RH} = 2$ carbethoxycyclo-pentanone.

b) Estimated by Baker (16) and Somarjai and Hornig (17).

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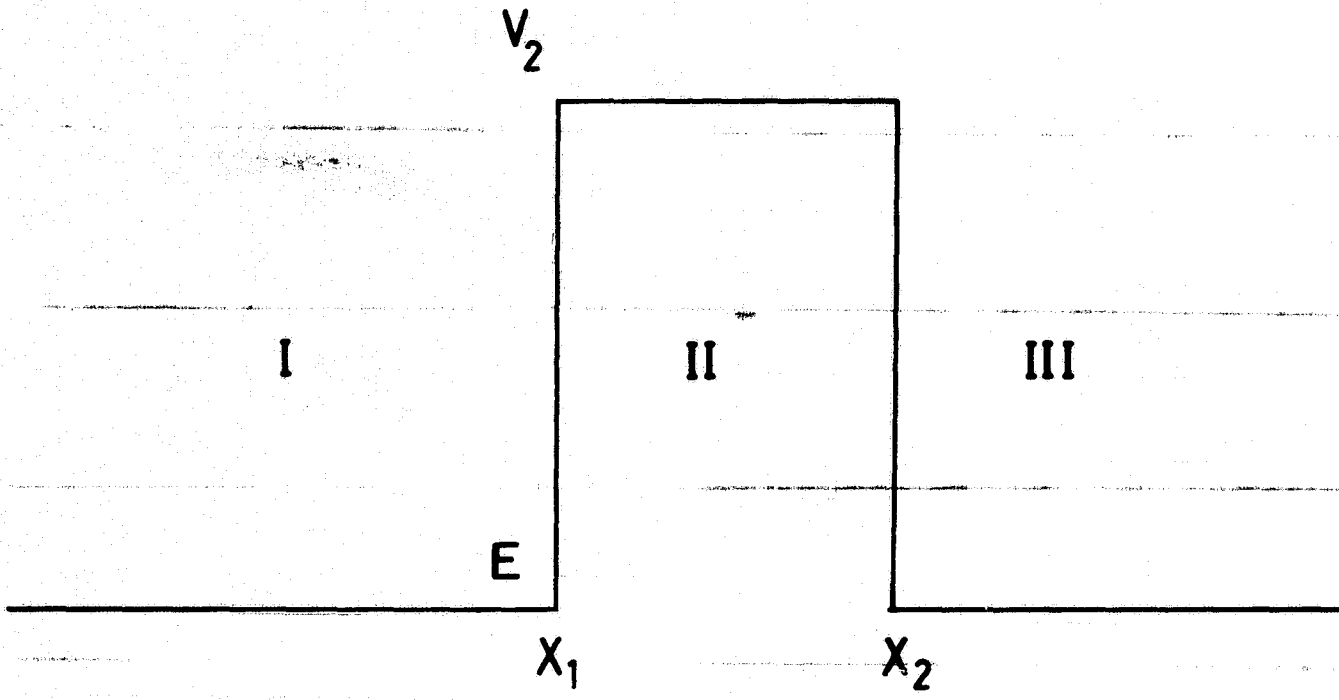


Figure 1.

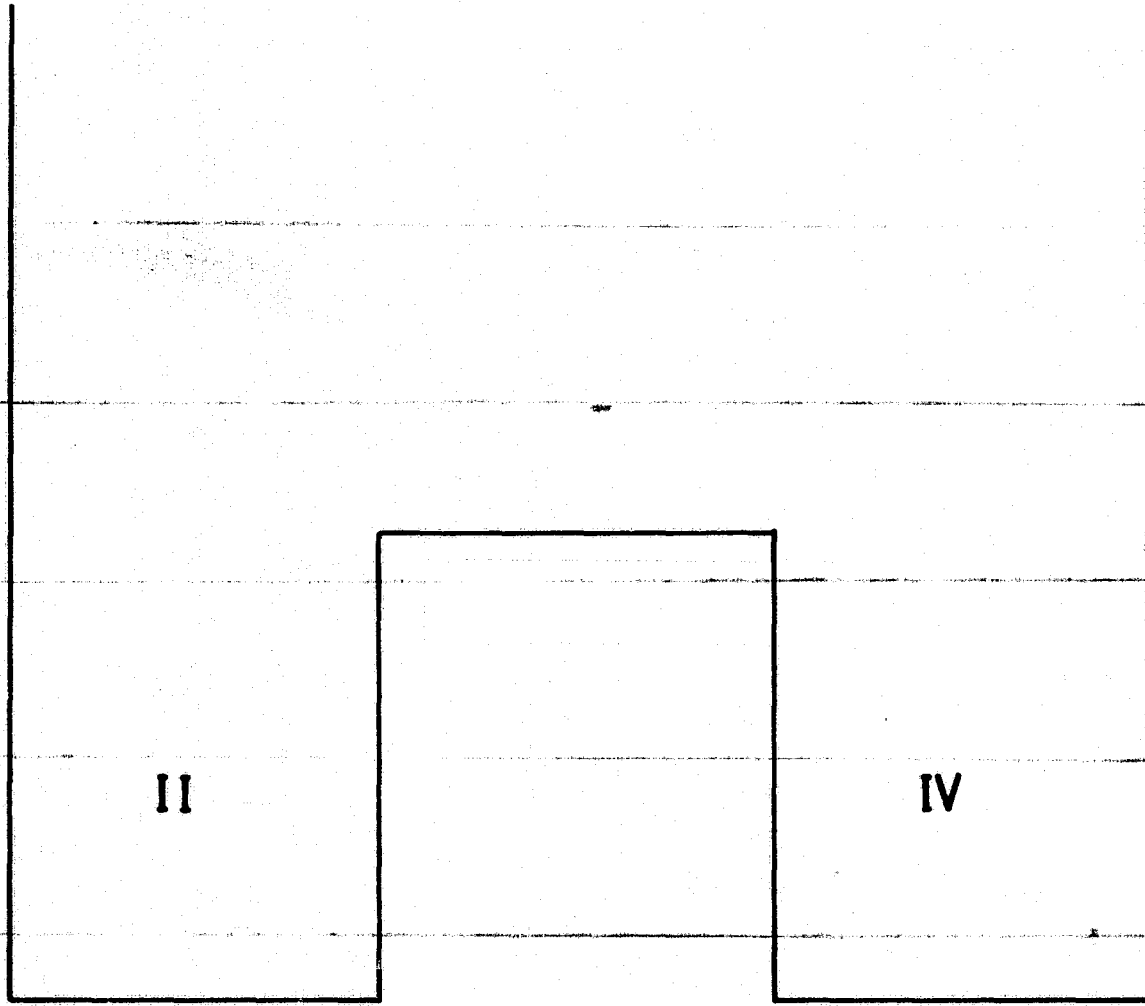


Figure 2.

ANNOTATIONS FOR FIGURES

Figure 1. Tunnelling through a square barrier.

Figure 2. Double well problem.

THEORY OF THE PROTON DISCHARGE PROCESS:

A BEBO CALCULATION

THEORY OF THE PROTON DISCHARGE PROCESS:

A BEBO CALCULATION

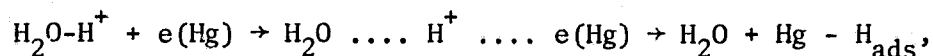
I. INTRODUCTION

The theory of proton discharge reaction formulated by Bockris and Matthews^{1,2} and Bockris, Srinivasan and Matthews³ considers the activated state to be formed from the excited vibration-rotation levels of the $\text{H}_2\text{O}-\text{H}^+$ bond. The LEP semi-empirical potential energy surface had been used to estimate the activation energy, separation factor, Tafel line and properties of the activated complex. However, newer criticisms of the LEP method by Johnston⁴ (difficulty of separating co-ordinates; observation of a minimum in the saddle point for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$), as well as the observation by Christov⁵ that the imaginary frequencies depend on the coulomb-exchange energy ratio, make an alternative approach to proton transfer calculations desirable.

The BEBO method⁶, on the other hand, is a fully empirical method (its empiricism depends on spectroscopic and thermodynamic parameters), not open to the criticisms made of the semi-empirical LEP method. This method has been developed in detail both for proton and hydrogen atom transfer processes in the gas phase with good success⁷. Some attempts have been made to use such a method for proton transfer in solution⁸.

II. THE BEBO METHOD

The BEBO method assumes that along the reaction co-ordinate the sum of the bond orders of the bond being broken and the bond being formed is always unit. Thus, for the rate-determining proton discharge step of the hydrogen evolution reaction on Hg, which may be written as:



the energy along the reaction co-ordinate may be written as^{11*}:

$$E = E_{\text{in}}^{\text{O}}(1-n^p) - E_{\text{fin}}^{\text{O}}(1-n)^q + BE_{\text{rep}}^{\text{O}}[n^\gamma(1-n)^\gamma], \quad (1)$$

where E_{in}^{O} , $E_{\text{fin}}^{\text{O}}$, $E_{\text{rep}}^{\text{O}}$ are the energies of the initial (H_3O^+ + e_{metal}), final ($\text{H}_{\text{ads}} + \text{H}_2\text{O}$) and repulsive ($\text{Hg} \dots \text{O}$) state^{**}; n is the bond order of the final state of index q . The parameters p and q are defined as⁹:

$$p = \frac{0.26 \ln(E_{\text{in}}^{\text{O}}/\epsilon_x)}{(R_{xy} - R_{\text{in}}^{\text{O}})}$$

and
$$q = \frac{0.26 \ln(E_{\text{fin}}^{\text{O}}/\epsilon'_x)}{(R'_{xy} - R_{\text{fin}}^{\text{O}})}$$

where R_{xy} , R'_{xy} and ϵ_{xy} and ϵ'_x are the internuclear separation and bond energy respectively in the corresponding noble gas diatomic cluster where $n = 0$. R_{xy} and ϵ_{xy} are for the initial state and R'_{xy} and ϵ'_x are for the final state.

γ and B are defined as:

$$\gamma = 0.26\alpha$$

$$\text{and } B = \exp[-\alpha\Delta R],$$

where α is the anharmonicity constant of the bond Hg-O and $\Delta R = [R_{\text{in}}^{\text{O}} + R_{\text{fin}}^{\text{O}} - R_{\text{rep}}^{\text{O}}]$, where R_{in}^{O} , $R_{\text{fin}}^{\text{O}}$ and $R_{\text{rep}}^{\text{O}}$ are the equilibrium internuclear separation of the bonds $\text{H}_2\text{O}-\text{H}^+$, M-H and Hg-O respectively.

* The initial state energy is submitted from the total energy in eqn. (1).

** By the repulsive state we mean the energy of interaction between Hg and the oxygen of the water molecule.

(a) Estimation of the various parameters of equation (1)

(i) Estimation of E_{in}^0 , E_{fin}^0 and E_{rep}^0 :

E_{in}^0 and E_{fin}^0 were taken from the estimation of Parsons and Bockris¹⁰, and Bockris and Matthews¹. They were -69kcal/mole for E_{in}^0 and -75kcal/mole for E_{fin}^0 at the reversible potential. E_{rep}^0 is the dissociation of the Hg ... O bond, and was taken as 80kcal/mole from the thermodynamic estimation of Solomon, Enke and Conway¹¹.

(ii) Estimation of γ and B:

The anharmonicity constant α is estimated from the equation:

$$\alpha = (F_{rep}^0 / 2E_{rep}^0)^{1/2} .$$

E_{rep}^0 is obtained from Badgers Rule. The value of α arrived at is 1.49\AA^{-1} . Thus,

$$B = \exp[-\alpha\Delta R_s] = 0.7335$$

where R_{in}^0 , R_{fin}^0 is estimated from Bockris and Matthews¹, and R_{rep}^0 is taken from Cotton and Wilkinson¹².

Moreover, $\gamma = 0.26\alpha = 0.3891$.

(iii) Estimation of p and q:

These are estimated from the equation given in the previous section and the values obtained are $p = 1.3$ and $q = 0.8$.

(b) Calculation of the activation energy at the reversible potential and the variation of the transfer coefficient with potential

Since p and q are both very near to unity, we can expand the first and second term of equation (1) in a Taylor series expansion, as suggested by Marcus⁸. Thus, we get:

$$E = (1-n)(E_{in}^0 - E_{fin}^0) - (p-1)nE_{in}^0 \ln n - E_{fin}^0 (q-1)1-n(\ln(1-n) + BE_{rep}^0 n^\gamma (1-n)^\gamma). \quad (2)$$

The activated state corresponds to the maximum of the E vs n curve given in equation (2). Thus, we differentiate E w.r.t. n and set it equal to zero.

Hence:

$$\frac{dE}{dn} = -Q = (p-1)E_{in}^0 (1 + \ln n) + (q-1)E_{fin}^0 [1 + \ln(1-n)] + \gamma BE_{rep}^0 n^{\gamma-1} (1-n)^{\gamma-1} (1-2n) = 0, \quad (3)$$

where $Q = (E_{in}^0 - E_{fin}^0)$.

Solving the above equation numerically gives us the value of n at the activated state. Let us denote this value of n as n^* . Thus, the activation energy now becomes:

$$E^* = Q(1-n^*) - (p-1)n^*E_{in}^0 \ln n^* - (1-n^*)E_{fin}^0 (q-1) \ln(1-n^*) + BE_{rep}^0 (n^*)^\gamma (1-n^*)^\gamma. \quad (4)$$

The transfer coefficient β is defined as the variation of the activation energy with respect to the reaction heat, Q, where $Q = Q_0 + e\eta$, and η is the overpotential. Thus:

$$\begin{aligned} \frac{d\Delta E^*}{dQ} = & (1-n^*) - (p-1)n^* \ln n^* + \frac{dn^*}{dQ} [-Q - (p-1)E_{in}^0 (1 + \ln n^*) + (q-1)E_{fin}^0 [1 + \ln(1-n^*)] \\ & + \gamma BE_{rep}^0 (n^*)^{\gamma-1} (1-n^*)^{\gamma-1} (1-2n^*)]. \end{aligned} \quad (5)$$

From (3) in (5):

$$= \frac{d\Delta E^*}{dQ} = (1-n^*) - (p-1)n^* \ln n^* = (1+n^*P). \quad (6)$$

Since, as the overpotential changes, E_{in}^0 changes*, the value of n^* , ΔE^* and β also change. Thus, using equations (3), (4) and (6), we are able to get the activation energy at the reversible potential, and the value of the

* E_{in}^0 comprises the energy of the H_3O^+ ion in the double layer and the energy of an electron in the metal, and is therefore potential dependent.

transfer coefficients for various overpotential. These results are summarized in Table (1) and the variation of β with overpotential is shown in Fig. 1.

(c) Calculation of the Quantum Mechanical Rate of the Reaction

Following Bockris and Matthews², we can write the quantum mechanical rate of the proton discharge reaction as:

$$i_q = k_1 C_{H_3O^+} \int_{E^0}^{\infty} W(E) e^{-(E-E^0)/kt} dE, \quad (7)$$

where k_1 is a constant (not a rate constant), $C_{H_3O^+}$ is the surface concentration of H_3O^+ ion per cm^2 , $W(E)$ is the proton tunneling probability, and E^0 is the zero point energy of the H_2O-H^+ bond. The corresponding classical current may be written as:

$$i_{Cl} = k_1 C_{H_3O^+} \cdot kT \exp[-(E^*-E^0)/kT]. \quad (8)$$

Thus, we can define:

$$\tau = \left(\frac{i_q}{i_{Cl}} \right) = \frac{1}{kT} \exp\left(\frac{E^* - E^0}{kT} \right) \int_{E^0}^{\infty} \exp[-(E-E^0)/kT] W(E) dE. \quad (9)$$

Let us define:

$$J_q = \int_{E^0}^{\infty} W(E) \exp[-(E - E^0)/kT] dE. \quad (10)$$

Thus, equation (9) becomes:

$$\tau = \left(\frac{i_q}{i_{Cl}} \right) = \frac{1}{kT} \exp\left(\frac{E^* - E^0}{kT} \right) J_q, \quad (11)$$

or

$$i_q = i_{Cl} \cdot \frac{1}{kT} \cdot \exp\left\{\frac{(E^* - E^0)}{kT}\right\} J_q. \quad (12)$$

To evaluate the current one must know the shape of the barrier along the one dimensional normal mode. The Eckart barrier appears to have the closest fit to the real barrier². It has the form:

$$V(x) = \frac{A \exp[2\pi x/d]}{1 + \exp[2\pi x/d]} + \frac{B \exp[2\pi x/d]}{\{1 + \exp(2\pi x/d)\}^2}, \quad (13)$$

$$\text{where } A = Q_0 + e\eta, \quad (14)$$

$$Q_0 = E_{(+\infty)} - E_{(-\infty)}, \quad (15)$$

$$B = 2E^* - A + 2\{E^*(E^* - A)\}^{1/2}, \quad (16)$$

$$\text{and } E^* = E_0^* - \beta e_0 \eta, \quad (17)$$

where $2d$ is the barrier width and E^* is the barrier height at $\eta = 0$.

Using equation (6) in equation (17):

$$E^* = E_0^* - (1 - n^{*P}) e_0 \eta. \quad (18)$$

For this barrier:

$$W(E) = \frac{\text{Cosh} 2\pi(\lambda + \mu) - \text{Cosh } 2\pi(\lambda - \mu)}{\text{Cosh } 2\pi(\lambda + \mu) + \text{Cosh } 2\pi\sigma}, \quad (19)$$

$$\text{where } \lambda = (d/h) (2m_{\text{eff}} \cdot E)^{1/2}, \quad (20)$$

$$\mu = (d/h) \{2m_{\text{eff}}(E - A)\}^{1/2}, \quad (21)$$

and

$$\sigma = \frac{1}{2} \left[\left(8m_{\text{eff}} d^2 \frac{B}{h^2} \right) - 1 \right]^{1/2}, \quad (22)$$

where m_{eff} is the effective mass of the tunneling particle along the reaction co-ordinate.

For barrier widths greater than 3\AA and $E_0^* \geq 1.0 \times 10^{-12}$ ergs we use the approximate formula:

$$W(E) = \frac{\exp\{2\pi(\lambda+\mu-\sigma)\} - \exp\{2\pi(\lambda-\mu-\sigma)\} - \exp\{-2\pi(\lambda-\mu+\sigma)\}}{1 + \exp\{2\pi(\lambda+\mu-\sigma)\}}. \quad (23)$$

(d) Effective Mass of the Tunneling Particle:

For a particle tunneling along the reaction co-ordinate, the system having a fixed centre of mass and constant angular variables, it was shown by Johnston that the effective mass of the particle along the reaction co-ordinate is different from the actual mass of the particle. Thus, Johnson⁹ shows that the tunneling particle has an effective mass, given as:

$$m_{\text{eff}} = \frac{m_A m_B (1+C^2) - m_H m_B C^2 + m_H m_A}{(m_A + m_B + m_H) (1+C^2)}, \quad (24)$$

where

$$C = \frac{dr_{A-H}}{dr_{H-B}}, \quad (25)$$

for a system of the form [A...H...B].

Christov and Georgiev¹³ have shown that under the limiting conditions, $m_H \ll m_A$ and $m_H \ll m_B$ are obtained from equation (24).

$$m_{\text{eff}} \approx \frac{1}{2} m_H. \quad (26)$$

In the system we are considering A is H₂O and B is Hg and the inequality $m_H \ll m_A$ and $m_H \ll m_B$ is evidently satisfied. Thus, in evaluating W(E) in equation (23), we use equation (26) to define the effective mass of the tunneling particle.

(e) The Separation Factor and its Variation with Potential

The hydrogen tritium separation factor is defined by the equation:

$$S_T = \left(\frac{C_H}{C_T} \right)_g / \left(\frac{C_H}{C_T} \right)_s ,$$

where $(C_H/C_T)_g$ and $(C_H/C_T)_s$ are the ratios of atomic concentration of hydrogen of tritium in the gas phase and in solution. The ratio $(C_H/C_T)_g$ is equal to twice the ratio of the velocities of H_2 and HT evolution since $C_{H_2} \gg C_{HT}$. Using the relation S_T may be expressed as:

$$S_T = \sigma \cdot \frac{\tau_H}{\tau_T} \cdot \frac{f_H^\ddagger}{f_T^\ddagger} \cdot \frac{f_{HTO,g}}{f_{H_2O,g}} \cdot K_T ,$$

where σ is a ratio of symmetry numbers

$$= S_{T,class} \frac{\tau_H}{\tau_T} . \quad (28)$$

Bockris, Srinivasan and Matthews³ showed that:

$$K_T (f_{HTO,g} / f_{H_2O,g}) = 316.46 .$$

It is assumed that the activated complex $H_2O \dots H \dots Hg$ (or its isotopic analogue) is similar to a linear triatomic molecule (cf. Parsons and Bockris¹⁰). Thus, $f_H^\ddagger / f_T^\ddagger$ is given by:

$$\frac{f_H^\ddagger}{f_T^\ddagger} = \frac{f_{H,t}^\ddagger}{f_{T,t}^\ddagger} \cdot \frac{f_{r,H}^\ddagger}{f_{r,T}^\ddagger} \cdot \frac{f_{vib,H}^\ddagger}{f_{vib,T}^\ddagger} . \quad (29)$$

Since the activated complex is regarded as immobile, the translational partition function ratio is unity. Bockris, Srinivasan and Matthews³

estimated the ratio of the rotational (around the axis) partition function ratio is:

$$\frac{f_{H,r}^\ddagger}{f_{T,r}^\ddagger} = \frac{I_H^\ddagger}{I_T^\ddagger} = 0.962 ,$$

where the I's are the amounts of inertia of the activated complex.

Moreover, they wrote the vibrational partition functions as:

$$\frac{f_{\text{vib},H}^\ddagger}{f_{\text{vib},T}^\ddagger} = \frac{\text{Sin } h (h\nu_T/2kT)_s}{\text{Sin } h (h\nu_H/2kT)_s} \cdot \frac{\text{Sin } h^2 (h\nu_T/2kT)_b}{\text{Sin } h^2 (h\nu_H/2kT)_b} . \quad (30)$$

The suffixes s and b stand for stretching and bending frequencies.

It was further shown that:

$$\frac{\text{Sin } h^2 (h\nu_T/2kT)_b}{\text{Sin } h^2 (h\nu_H/2kT)_b} = \frac{m_H}{m_T} = \frac{1}{3} . \quad (31)$$

For calculating of the stretching vibrational frequencies, it is necessary to solve the secular equation:

$$\lambda^2 - \lambda \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right) F_{11} + \left(\frac{1}{m_2} + \frac{1}{m_3} \right) F_{22} - \frac{2}{m_2} F_{12} \right] + \frac{m_1 + m_2 + m_3}{m_1 m_2 m_3} (F_{11} F_{22} - F_{12}^2) = 0, \quad (32)$$

where F_{11} is the force constant of the bond between m_1 and m_2 , F_{22} is the force constant of the bond between m_2 and m_3 , and F_{12} is the coupling force constant. λ is given by the expression:

$$\lambda = 4 \pi^2 \nu^2 . \quad (33)$$

Bockris, Srinivasan and Matthews³ used an LEP surface to estimate the force constant. We will estimate it from the BEBO calculations.

In the BEBO method, if we define the force constant along the reaction co-ordinate to be F_ρ and that perpendicular to it to be F_σ , then F_ρ and F_σ are given as⁹:

$$F_\rho = \frac{10.7}{\frac{1}{n^{*2}} + \frac{1}{(1-n^*)^2}} \left[\frac{E_{in}^0 p(p-1)}{(n^*)^{2-p}} + \frac{E_{fin}^0 q(q-1)}{(1-n^*)^{2-q}} + \frac{E_{rep}^0 2B}{(n^*)^\gamma (1-n^*)^\gamma} \left(1 + \frac{(1-\gamma)(1-2n^*)^2}{2n^*(1-n^*)} \right) \right] \quad (34)$$

and

$$F_\sigma = \frac{F_{in}^0 n^3 + F_{fin}^0 (1-n^*)^3 + (F_{rep}^0/2) (n^*)^\gamma (1-n^*)^\gamma B}{(n^{*2} + (1-n^*)^2)}, \quad (35)$$

where F_{in}^0 , F_{fin}^0 and F_{rep}^0 are the force constants of the initial, final and the repulsive states.

To solve equation (32) we have to have the force constants in valence bond co-ordinates, with the force constants F_{11} , F_{22} and F_{12} . The following relation holds⁹ between F_{11} , F_{22} and F_{12} , and F_ρ and F_σ .

$$F_{11} = \frac{F_\rho (1-n^*)^2 + F_\sigma n^{*2}}{(n^*)^2 + (1-n^*)^2}, \quad (36)$$

$$F_{22} = \frac{F_\rho (n^*)^2 + F_\sigma (1-n^*)^2}{(n^*)^2 + (1-n^*)^2}, \quad (37)$$

$$F_{12} = \frac{(-F_\rho + F_\sigma) n^* (1-n^*)}{(n^*)^2 + (1-n^*)^2}. \quad (38)$$

Thus, knowing n^* , F_ρ and F_σ we obtain F_{11} , F_{22} and F_{12} . Thus, we solve equation (32) to obtain the vibrational frequencies of the activated state and the ratio of the vibrational partition function given by equation (3). The results are tabulated in Table (2).

(f) Estimation of τ_H/τ_T and the Tafel lines:

Equation (10) was solved by doing a numerical integration, taking the expression given by equation (23) for $W(E)$ on an IBM 1130 digital computer for various values of the width of the barrier. The dependence of the results upon the width of the barrier is shown in Fig. (2). The most probable parameters were selected on the basis that they give good agreement with (a) Tafel slope, (b) Activation energy, and (c) The variation of the separation factor with potential. Thus, the Tafel lines obtained for the most probable barrier parameters are shown in Fig. 3a and b and the data are summarized in Table 3. The variation of the separation factor with potential is shown in Fig. (4). The theoretical calculation was not pursued at higher overpotentials due to limitations of the programme. However, the calculations are bound to show a constancy of s with η at sufficiently high η 's, because when the barrier has been made sufficiently low by increasing η the quantal contribution becomes negligible.

III. CONCLUSIONS

Thus, in this article, we have shown that the BEBO method applied to the electrolytic hydrogen evolution, gives:

(a) Excellent agreement on the variation of the transfer coefficient with potential.

(b) Good agreement with the experimental Tafel slopes.

(c) Tafel lines which show the occurrence of barrierless discharge at high overpotentials.

(d): Good agreement between the theoretical and experimental separation factor values and their variation with potential.

TABLE I

VARIATION OF THE TRANSFER COEFFICIENT WITH POTENTIAL

| η | $(\Delta H^*)_{\text{calc}}$ (kcal/mole) | $(\Delta H^*)_{\text{expt}}^2$ (kcal/mole) | β |
|--------|---|---|---------|
| 0.0 | 15.54 | 20 | 0.561 |
| 0.25 | | | 0.558 |
| 0.5 | | | 0.554 |
| 0.8 | | | 0.551 |
| 0.9 | | | 0.547 |
| 1.0 | | | 0.591 |
| 1.25 | | | 0.531 |
| 1.5 | | | 0.52 |
| 1.63 | | | 0.48 |

TABLE 2

| $K_T \cdot \frac{f_{HTO,g}}{f_{H_2O,g}}$ | $\frac{f_{r,H}^\dagger}{f_{r,T}^\dagger}$ | F_σ dyns/cm | F_ρ dyns/cm | W_H $\times 10^{13}$ sec ⁻¹ | W_T $\times 10^{13}$ sec ⁻¹ | $\frac{(f_{vib,H}^\dagger)_b}{(f_{vib,T}^\dagger)_b}$ | (S_{H_T}) class |
|--|---|-----------------------|---------------------|--|--|---|-------------------|
| 316.46 | 0.962 | 3.65×10^5 | -2.6×10^5 | 6.35 | 1.53 | 0.021 | 3.6 |

TABLE 3

TAFEL LINE AND THE VARIATION OF SEPARATION FACTOR WITH POTENTIAL

$$E_o^* = 1.6 \times 10^{-12} \text{ ergs, } A_o = 0.6 \times 10^{-12} \text{ ergs, and } 2d = 4.5\text{\AA} .$$

| η (in ergs) | η (in volts) | $Jq(H^+)$ | $Jq(T^+)$ | $T_{H/T}$ | $S_{H/T}$ |
|-----------------------|-------------------|--------------------------|--------------------------|-----------|-----------|
| 0.00 | | | | | |
| 0.4×10^{-12} | 0.25 | 0.5857×10^{-12} | 0.1386×10^{-13} | | |
| 0.8×10^{-12} | 0.5 | 0.1080×10^{-9} | 0.3251×10^{-11} | 29 | 10.15 |
| 1.2×10^{-12} | 0.8 | 0.1843×10^{-7} | 0.5442×10^{-9} | 2.4 | 8.40 |
| 1.4×10^{-12} | 0.9 | 0.2150×10^{-6} | 0.6769×10^{-8} | 2.25 | 7.85 |
| 1.6×10^{-12} | 1.0 | 0.2228×10^{-5} | 0.7483×10^{-7} | 2.07 | 7.24 |
| 1.8×10^{-12} | 1.13 | 0.2455×10^{-4} | 0.8866×10^{-6} | | |
| 2.0×10^{-12} | 1.25 | 0.2166×10^{-3} | 0.8399×10^{-5} | 1.55 | 5.4 |
| 2.4×10^{-12} | 1.5 | 0.1998×10^{-1} | 0.1148×10^{-2} | 1.2 | 4.20 |
| 2.6×10^{-12} | | 0.4091×10^{-1} | 0.4980×10^{-2} | | |
| 2.8×10^{-12} | | 0.4300×10^{-1} | 0.2769×10^{-1} | | |

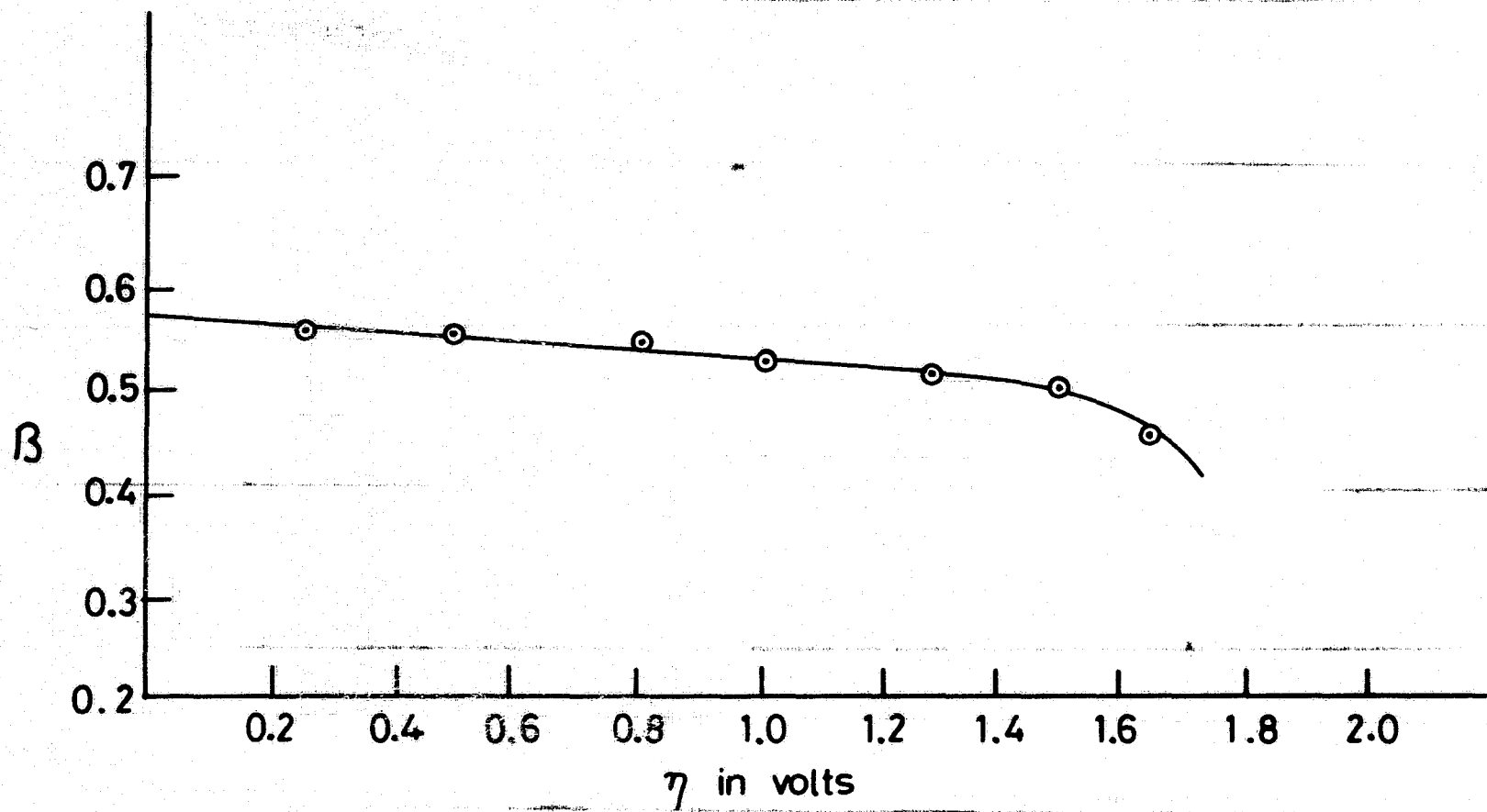


Figure 1.

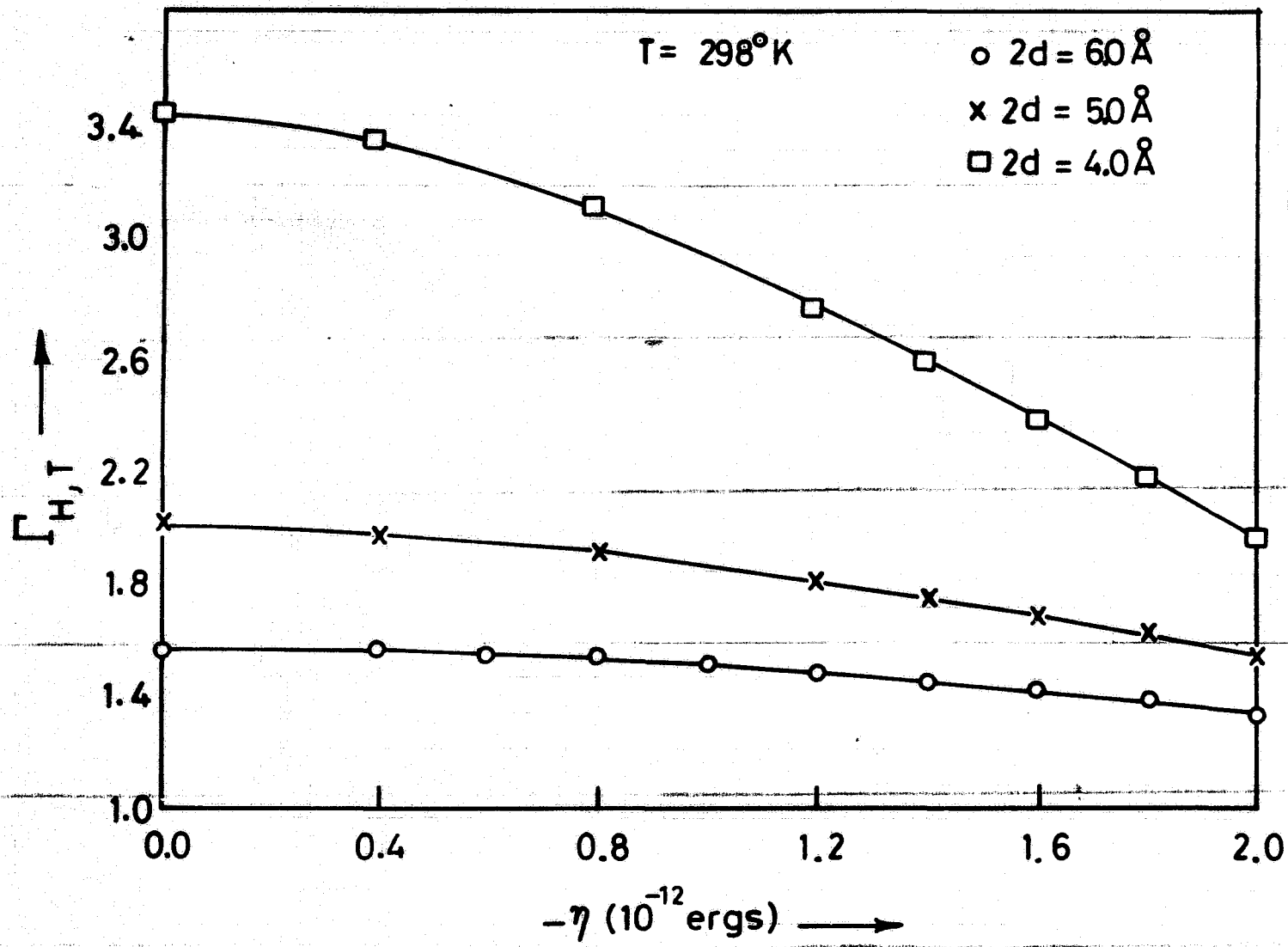


Figure 2.

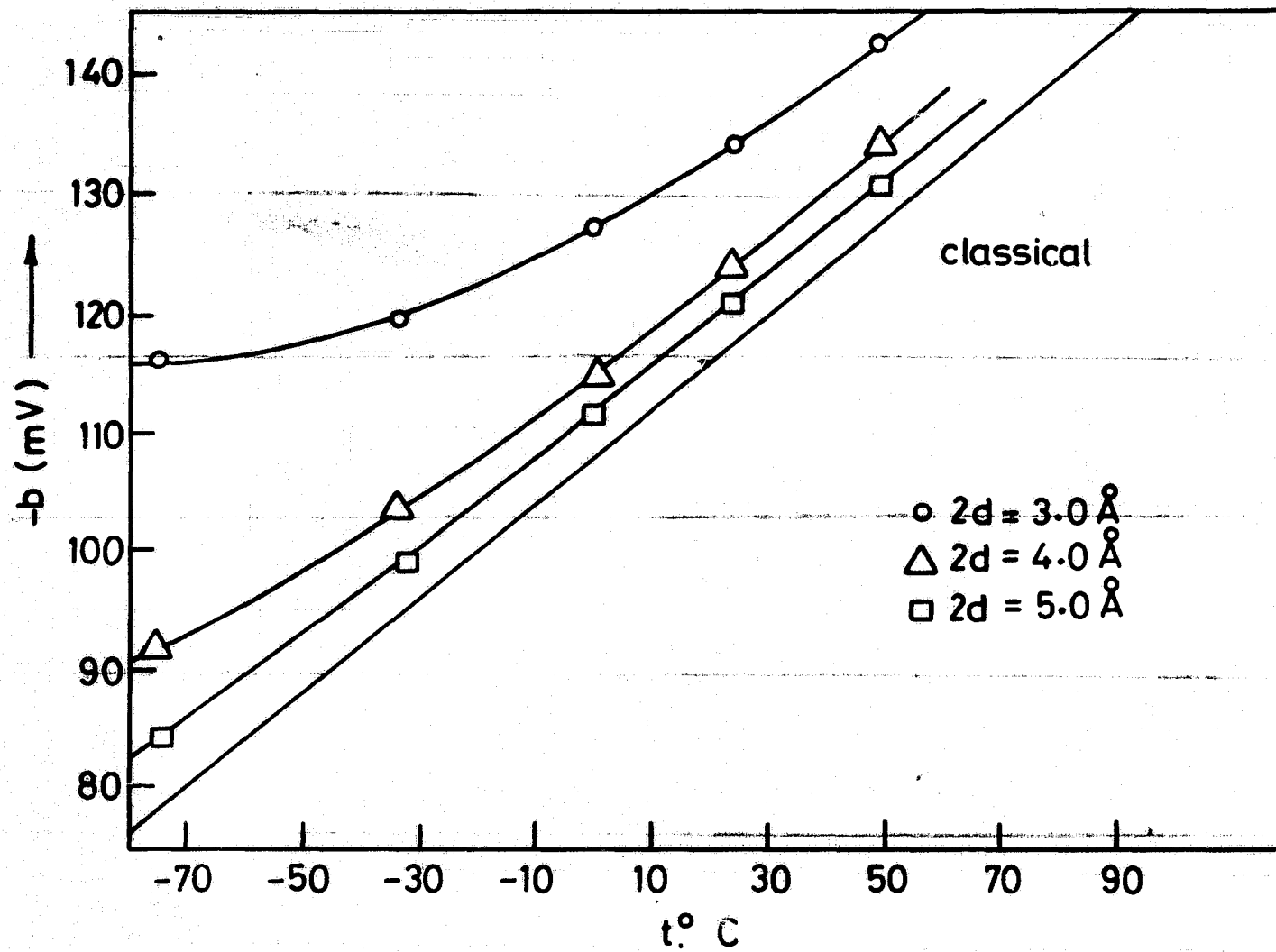


Figure 3.

—△—△ Tritium discharge.

—○—○ Proton discharge.

Slopes,

(a) Proton discharge = 118 mV.

(b) Tritium discharge = 117 mV.

Experimental slope \approx 120 mV.

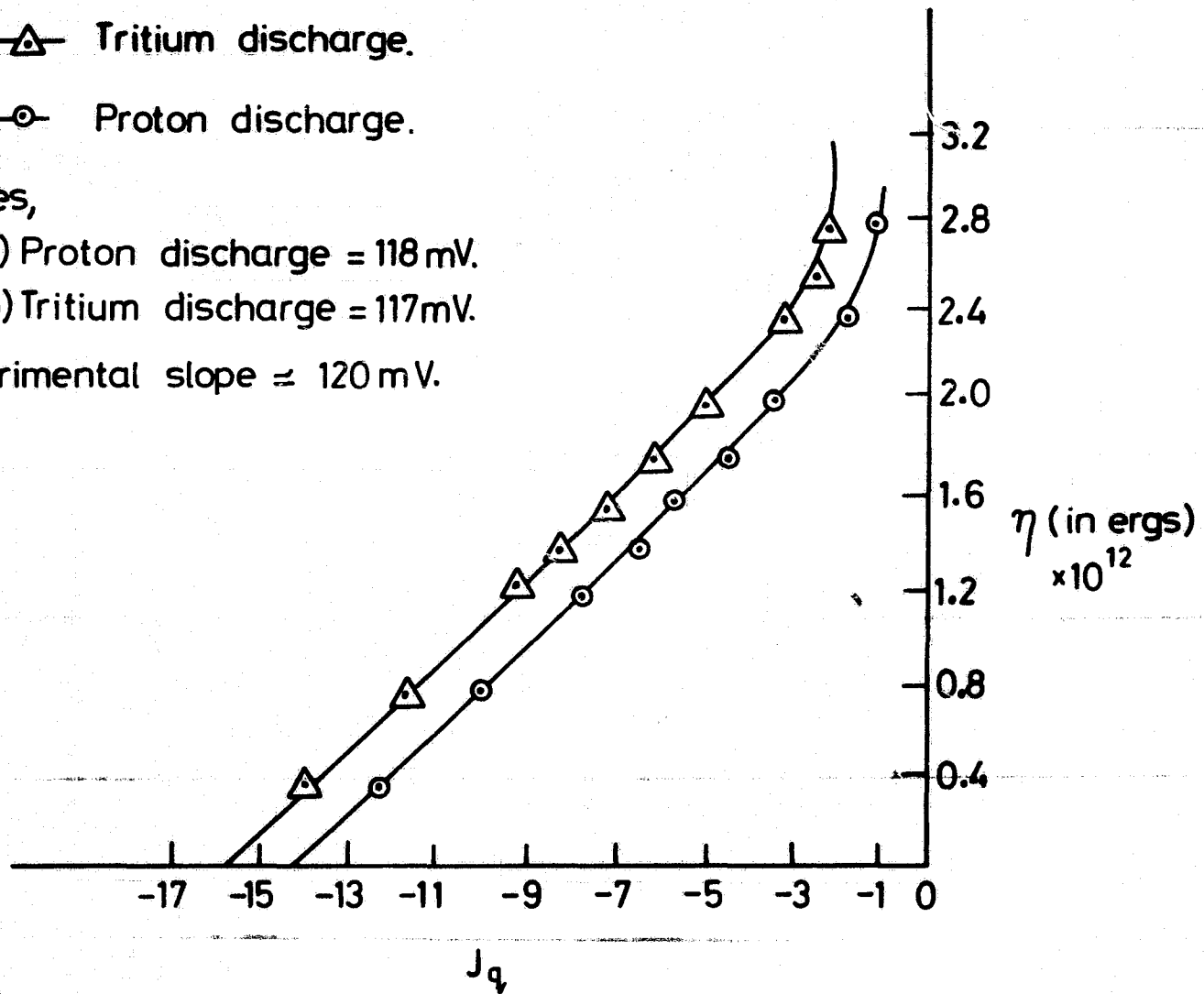


Figure 3b.

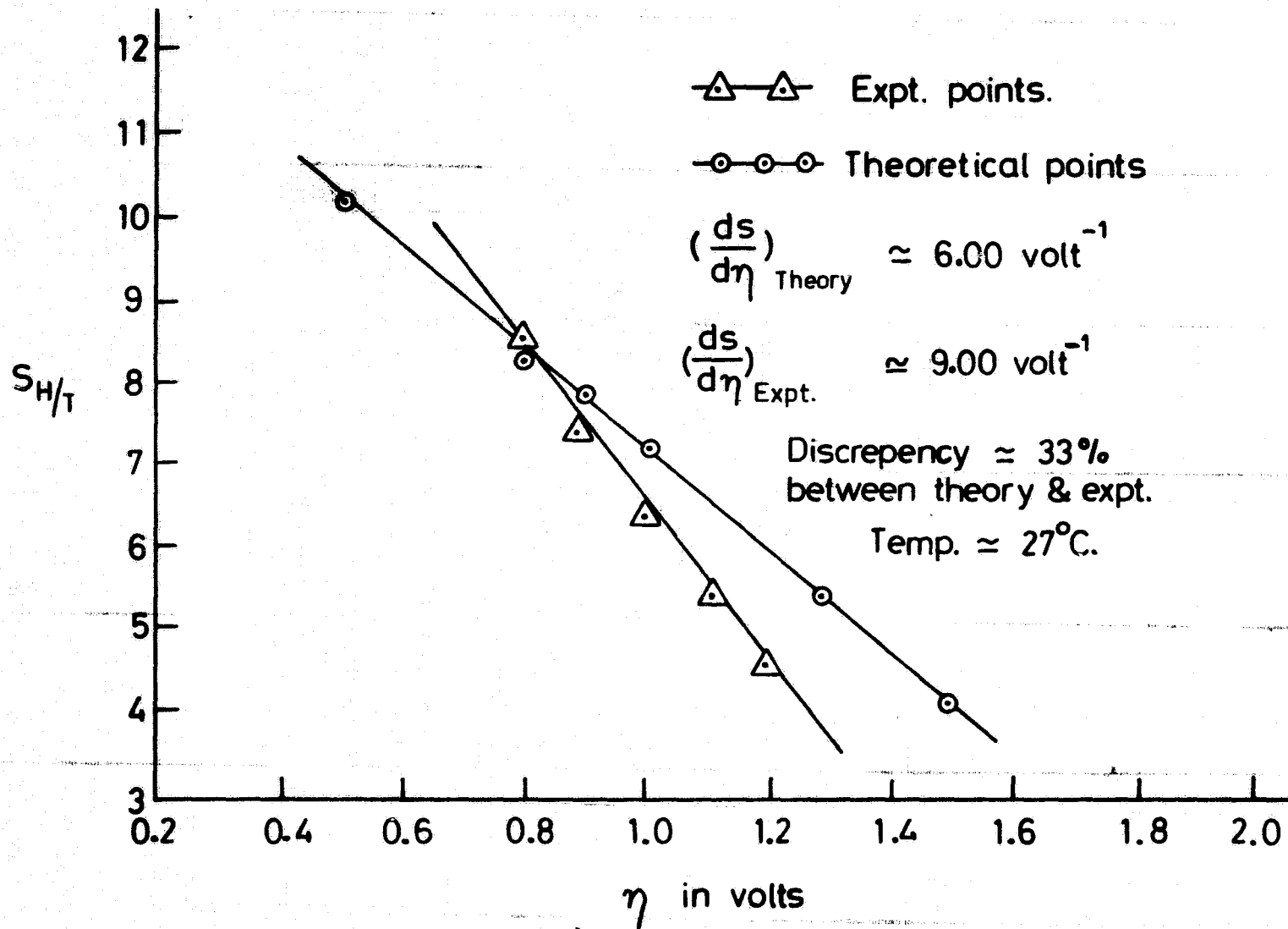


Figure 4.

ANNOTATIONS FOR FIGURES

- Figure 1. Variation of β with overpotential η .
- Figure 2. (a) Tafel lines for various barrier parameters.
 (b) Variation of the separation factor with potential.
- Figure 3. Variation of J_q (the quantum mechanical correction to Tafel line), for most probable barrier parameter.
- Figure 4. Variation of separation factor with overpotential for most probable barrier parameters.

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ON ALTERNATIVE ACTIVATION MECHANISMS IN ELECTRON TRANSFER

REACTIONS IN SOLUTION

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REACTIONS IN SOLUTION

Summary

The model for electron-transfer kinetics in solution is considered. In one model, the appropriate energetic condition for charge transfer is met by a small number of vibration-rotation states, in thermal equilibrium with the solution. Collisional activation (CA) between ion in the solution and the solvent is the origin of such states. In another model (EF), CA is neglected, and the appropriate energy states are regarded as being reached by the fluctuations in the energy of the ion, as a result of its interaction with many surrounding solvent molecules. The methodology of deduction of the dependence of the charge-transfer rate upon the interfacial potential difference for the two models is outlined. CA suggests a linearity of $\log R$ with η (R = rate; η = overpotential). There is no linear region suggested on the EF model, although such relations are regularly observed. This lack of consistence arises because the perturbations which are regarded as the origin of activation in EF are simple harmonic. This is an intrinsic part of the model of EF, not as an approximation within it. Correspondingly, a comparison of $(\Delta F_{\text{calc}}^{\text{ox}})_{\text{EF}}$ with experiment shows inconsistencies.

Comparison with spectroscopic data for H_2O^+ in solution suggests that the energy distribution in the vibration-rotation levels in this ion is continuous and that classical modes of vibration exist in water. A supposed discontinuity, - which would have annulled the deduction of Tafel's law, - was an origin of the EF model.

In the EF model, the applicability of the Born-Landau equation, $F^0 = e^2/2r(1/\epsilon_{\text{opt}} - 1/\epsilon_{\text{stat}})$ is assumed. However, the applicability depends on a sufficiently large difference of the energy of an electron, trapped in the medium and bound to atoms in it. This difference is great if the medium is a solid, but not if it is a liquid.

States suitable for acceptance or donation of electrons from ions to metals arise (at the equilibrium potential) much more frequently as a result of the equilibrium of the H_2O^+ ion with the solvent heat sink than those by electrostatic fluctuation.

I. INTRODUCTION

A quantum mechanical formulation of the rate of electron transfer reactions in solution was first given by Gurney¹ (1931). This model (termed here the collisional activation model (CA)) was further developed by Butler², Christov⁴, Gerischer³, and by Bockris and Matthews⁵. The essence of this approach is that a thermal equilibrium between the vibration-rotation levels of the solvated ions and the thermal energy of the solvent is assumed.

Weiss⁶, and Platzman and Franck⁷, founded another model which they assumed that the energy of activation arises from some undefined movements in the continuum solvent. It was elaborately developed by Marcus⁸, considering non-equilibrium dielectric polarization changes in a continuum solvent. A molecular model for this type of activation process was described in detail by Levich⁹, and by Dogonadze¹⁰, where it was stated that the fluctuations in the electrostatic energy arising from the libratory movement of the solvent dipoles cause the activation of the

reactant ion. This model will be referred to as the Energy Fluctuation (EF) model.

In this article, we attempt to distinguish between these two models. The collisional-activation model is an application to electron transfer kinetics of the concepts of thermal distribution of vibrational states, as discussed in the reaction rate theory of gas phase reactions. The electrostatic fluctuation approach differs fundamentally from previous models of reactions in solution.

II. THE TWO MODELS

In both approaches a radiationless electron transfer is assumed and the Born-Oppenheimer approximation is invoked to separate the coordinates of the fast moving electron and the slow moving heavy particles, e.g., the solvent molecules. The continuum electrostatic approach uses a double adiabatic approximation by which it separates the co-ordinates of the electron, the proton, and the solvent molecules.

In considering the hydrogen evolution reaction, both models calculate the quantum mechanical probability of protons leaking through the barrier. However, they differ in the methodology of evaluating the transition probability. In the thermal approach, the WKB tunneling theory is used⁵, whereas in the electrostatic continuum approach, the use of time-dependent perturbation theory is advocated⁹, although the barrier has usually been considered transparent to protons.

In the CA model it is assumed that there is a classical distribution of vibration-rotation levels in the ion-solvent complex (because of the increase in the number of such levels in solution, compared to that in the

gas phase). Furthermore, for a reaction like the hydrogen evolution reaction, the CA model assumes that the H_3O^+ ion in the excited vibration-rotation levels produces the "activated state" for the reaction. In the "activated state", quantum levels for electrons exist in the H_3O^+ ion which are equal in energy to the energy of mobile electrons in the metal, and consequently a radiationless electron transfer occurs.

The quantum properties of the proton (in reactions such as $\text{H}_3\text{O}^+ + e \rightarrow \text{H}_{\text{ads}}$) are accounted for by assuming that protons have a probability of permeating the energy barrier between it and the metal. A Gamow type tunneling equation is used for the probability of penetration*.

At present, theories of chemical reaction in the gas phase assume that the small number of excited bonds are the medium of the reaction. (The type of model is assumed in the CA approach). Exactly analogous concepts are used to explain the mechanism of reactions in solution. However, the EF model differs from these available theories. Here, it is assumed without argument that the number of excited levels is too small (at room temperature) to be kinetically significant. For a radiationless electron transition, however, there

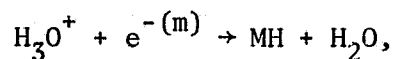
* An objection¹⁰ has been made to the use of a one-dimensional WKB approximation in calculating a transition probability. Thus, it is claimed that the WKB method calculates transition through a stationary barrier. However, the transitions involved in the proton discharge process are non-stationary in nature. Time-dependent perturbation theory should clearly be used. However, it can be shown¹⁷ that, when it is applied, then, for the time domain concerned in chemical kinetics, it gives approximately the WKB approximation.

must be an excitation of the electronic energy level in the acceptor so that it becomes equal to the energy of the Fermi level in the metal. To achieve this, the electronic energy of the reacting ion is pictured as experiencing a fluctuation in its energy with respect to the solvent dipoles in the bulk of the solution.

III. A DEDUCTION OF THE RATE-OVERPOTENTIAL RELATION ACCORDING TO BOTH MODELS

1. The Collisional-Activation Model

Considering the discharge reaction,



the quantum mechanical rate may be written as:

$$i = eC_{\text{H}^+} \int_x \int_{\epsilon} n(\epsilon_i) \rho(\epsilon_i) W_{if}(\epsilon_i, x) d\epsilon_i dx, \quad (1)$$

where C_{H^+} is the surface concentration of the proton, $n(\epsilon_i)$ is the Fermi distribution of electrons in the metal, $\rho(\epsilon_i)$ is the density of states and $W_{if}(\epsilon_i)$ is the transition probability for the whole reaction. Now, $W_{ia}(\epsilon_f)$ using the adiabatic approximation, may be split into two parts: (a) the probability of electron tunneling, $P(\epsilon_i, x)$; and (b) the probability of proton transfer across or over the barrier, $W(\epsilon_i, x)$. Thus, we can rewrite equation (1) as:

$$i = eC_{\text{H}^+} \int_x \int_{\epsilon} n(\epsilon_i) \rho(\epsilon_i) P(\epsilon_i, x) W(\epsilon_i, x) d\epsilon_i dx. \quad (2)$$

If we make the assumption that the transition occurs from a fixed distance essentially (i.e., the OHP), we can get rid of the integration over x . Hence:

$$i = eC_{H^+} \int_{\epsilon_0}^{\infty} P(\epsilon_i) n(\epsilon_i) \rho(\epsilon_i) W(\epsilon_i) \exp\left[-(\epsilon_i - \epsilon_0)/kT\right] d\epsilon_i, \quad (3)$$

where $W(\epsilon_i)$ is the probability of proton tunneling at an energy level ϵ_i , ϵ_0 is the zero point energy level for the H_3O^+ ion.

In the adiabatic case, where the electron transfer probability is unity, the equation reduces to:

$$i = eC_{H^+} \int_{\epsilon_0}^{\infty} n(\epsilon_i) \rho(\epsilon_i) W(\epsilon_i) \exp\left[-\frac{(\epsilon_i - \epsilon_0)}{kT}\right] d\epsilon_i. \quad (4)$$

Using the free electron approximation, for metals, we can write:

$$\rho(\epsilon_i) = \frac{mV_e}{2\pi^2 h^3} \{2m(\epsilon_i - u_0)\}^{1/2}, \quad (5)$$

where V_e is the average volume occupied by one electron, and $n(\epsilon_i)$ we substitute the Fermi distribution:

$$n(\epsilon_i) = \left[\exp\left(\frac{\epsilon_i - \epsilon_F}{kT}\right) + 1 \right]^{-1}. \quad (6)$$

Using (5) and (6) in (4) we get:

$$i = eC_{H^+} \int_{\epsilon_0}^{\infty} \left[\exp\left(\frac{\epsilon_i - \epsilon_F}{kT}\right) + 1 \right]^{-1} \cdot \frac{mV_e}{2\pi^2 h^3} \{2m(\epsilon_i - \epsilon_0)\}^{1/2} W(\epsilon_i) \exp\left[-(\epsilon_i - \epsilon_0)/kT\right] d\epsilon_i. \quad (7)$$

A problem is to evaluate $W(\epsilon_i)$, the proton transfer probability. It depends on approximating the actual potential energy barrier by a barrier of similar shape for which $W(\epsilon_f)$ has a known solution. The Eckart barrier⁵ resembles such a barrier. The unsymmetrical Eckart barrier is given by:

$$V(x) = \frac{A \exp(2x/d)}{1 + \exp(2x/d)} + \frac{B \exp(2x/d)}{1 + \exp(2x/d)^2}, \quad (8)$$

where $2d$ is the barrier width, A is the energy difference between the potential energy minimum, and B is defined by:

$$B = 2\epsilon_f - A + 2\left[\epsilon_i \cdot (\epsilon_i - A)\right]^{1/2}.$$

For the hydrogen evolution reaction (HER) we may write:

$$\begin{aligned} A &= A_0 = \epsilon_0 \\ \epsilon &= \epsilon_0 + \beta e_0 \eta. \end{aligned} \quad (8a)$$

For the barrier represented by (8), the tunneling probability is:

$$W(\epsilon_i) = \frac{\text{Cosh } 2\pi(\lambda + \mu) - \text{Cosh } 2\pi(\lambda - \mu)}{\text{Cosh } 2\pi(\lambda + \mu) + \text{Cosh } 2\pi\sigma}, \quad (9)$$

where

$$\begin{aligned} \lambda &= (d/h) (2m\epsilon_i)^{1/2} \\ \mu &= (d/h) \left[2m(\epsilon_i - A) \right]^{1/2} \\ \sigma &= \left(\frac{1}{2} \right) \left[\left(8md^2 B / h^2 \right) - 1 \right]^{1/2}. \end{aligned}$$

Introducing $W(\epsilon_i)$ in (7) yields:

$$i = eC_H \int_{\epsilon_0}^{\infty} \left(\exp\left(-\frac{\epsilon_i - \epsilon_F}{kT}\right) + 1 \right)^{-1} \frac{mV}{2\pi^2 \hbar^3} \left[2m_e (\epsilon_i - u_0)^{\frac{1}{2}} \right] \frac{\text{Cosh}2\pi(\lambda+\mu) - \text{Cosh}2\pi(\lambda-\mu)}{\text{Cosh}2\pi(\lambda+\mu) + 2\pi\alpha} \exp\left[-\frac{(\epsilon_i - \epsilon_0)}{kT}\right] d\epsilon_i . \quad (10)$$

The activation overpotential, η , is included in ϵ_i . In a numerical solution, made by Bockris and Matthews⁵, the barrier parameters were taken as those which produced a consistent Tafel line and was also consistent with the variation of the H/T separation factor with potential⁵.

2. The Electrostatic Fluctuation Approach¹⁰

Using the Fermi Golden Rule of second-order perturbation theory, a general expression for the transition probability may be written as:

$$W_{if}(\epsilon_i) = \frac{2\pi}{\hbar} A_v \sum_f \int |\Psi_f^* \nu \Psi_i| dv|^2 \delta(E_i - E_f) , \quad (11)$$

where Ψ_i and Ψ_f are the initial and final state wave functions, ν is the perturbation operator, and $\delta(E_i - E_f)$ is the dirac-delta function.

For any electron transfer reactions, in the adiabatic approximation, the initial and final state wave functions can be written as the product of the electronic and the solvent wave function in each of these states respectively. Thus:

$$\Psi = \phi(r, R) \chi(R) , \quad (12)$$

where ϕ is the wave function of the fast sub-system, i.e., the electron, and χ is the wave function of the slow sub-system, i.e., the solvent molecules, r and R are the electronic and solvent co-ordinates, respectively.

Thus, equation (11) can be written as:

$$W_{if} = \frac{2\pi}{\hbar} \text{Av} \sum_f \left| \int \phi_f^*(\mathbf{r}, \mathbf{R}) \chi_f^*(\mathbf{R}) v(\mathbf{r}, \mathbf{R}) \chi_i(\mathbf{R}) \phi_i(\mathbf{r}, \mathbf{R}) d\mathbf{r} d\mathbf{R} \right|^2 \delta(E_f - E_i). \quad (13)$$

Since the wave function of the heavy particles is localized in space, whereas the wave function $\phi(\mathbf{r}, \mathbf{R})$ and the perturbation energy $v(\mathbf{r}, \mathbf{R})$ are distributed over the whole volume, we can write equation (13) as:

$$W_{if}(\epsilon_i) = \frac{2\pi}{\hbar} \text{Av} \sum_f \left| \int \phi_f^* v \phi_i d\mathbf{r} \right|^2 \left| \int \chi_f^* \chi_i d\mathbf{R} \right|^2 \delta(E_f - E_i). \quad (14)$$

Defining $L = \left| \int \phi_f^* v \phi_i d\mathbf{r} \right|$, we get:

$$W_{if}(\epsilon_i) = \frac{2\pi}{\hbar} L^2 \text{Av} \sum_f \left| \int \chi_f^* \chi_i d\mathbf{R} \right|^2 \delta(E_f - E_i). \quad (15)$$

Taking the Fourier expansion of the delta function, equation (15) may be rewritten as:

$$W_{if}(\epsilon_i) = \frac{1}{h^2} L^2 \text{Av} \int_{-\Delta}^{+\infty} \left| \int \chi_f^* \exp\left(\frac{i}{\hbar}(H_f - H_i)t\right) \chi_i \right|^2 dt. \quad (16)$$

To solve this matrix element, we have to define H_i and H_f , which are Hamiltonians of the initial and final states. Thus, we need a Hamiltonian for the initial and final states. The Hamiltonian may be written as:

$$H_\alpha = H_e + H_s + V_{e,s},$$

where $\alpha = i, f$, H_e is the Hamiltonian for the kinetic energy of the electron, H_s is the Hamiltonian for the polar solvent and $V_{e,s}$ is the interaction between the electron and the solvent.

Levich⁹ has suggested the Hamiltonian for the solvent H_s may be written as:

$$H_s = \sum \frac{\hbar\omega_0}{2} \left(q_k^2 - \frac{\partial}{\partial q_k} \right) . \quad (17)$$

The next problem is then to evaluate $V_{e,s}$. The electrostatic approach¹⁰ considers the hydrated ion to be surrounded by dipoles. We may divide the dipoles of the solvent into two groups: (1) molecules which are arranged closely around the ion and form the so-called inner hydration sphere; and (2) all the remaining solvent continuum. However, the electrostatic fluctuation approach neglects the interaction between the ion and the inner solvation sheath, because the energy of interaction for the ion and the inner layer is such that for these bonds $\hbar\omega_i \gg kT$. Thus, this approach, instead of looking for a Hamiltonian comprising of specific interactions, with the ion and the inner sphere, considers only the long range interaction between the electron in the ion and the continuum solvent. This interaction between the electron and the far off dipoles in the solvent is small. However, from time to time, a fluctuation from the normal distribution will occur (see Section IV). It has been assumed that such fluctuations occur with a frequency sufficient to rationalize observed rates. Using macroscopic dielectric theory, we can therefore write:

$$V_{es} = \int D_e (P_{in} + P_{non-in})_{long} dV , \quad (18)$$

where D_e is the induction of the electron field, P_{in} and P_{non-in} represents the inertial and non-inertial part of the polarization, the subscript "long" indicates that the interaction is only with the longitudinal component of the wave.

Now, solving (16) using a harmonic oscillator wave function¹¹ and averaging the matrix element using Feynman's method, one obtains:

$$W_{if}(\epsilon_i) = |L|^2 \left(\frac{\pi}{\hbar E_s} \right)^{1/2} \exp - \left(\frac{(J_f - J_i + E_s)^2}{4E_s kT} \right), \quad (19)$$

where J_f and J_i are the ground state energies of the initial and final states and E_s the repolarization energy is defined as:

$$E_s = (\hbar\omega_o/2) \Sigma (q_{ki}^{(o)} - q_{kf}^{(o)})^2, \quad (20)$$

where ω_o is the librational frequency of the solvent dipoles. The quantity E_s is a crucial quantity of the electrostatic continuum theory. However, it cannot be evaluated from equation (20) which is the quantum mechanical solution. Thus, in EF model, the basic quantity E_s is evaluated from classical macroscopic dielectric theory. Thus:

$$E_s = \left(\frac{\hbar\omega_o}{2} \right)_k \left(q_{ki}^{(o)} - q_{kf}^{(o)} \right)^2 = (ne)^2 \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right) \left(\frac{1}{2a_1} - \frac{1}{2a_2} - \frac{1}{R} \right), \quad (21)$$

where a_1 and a_2 are the radius of the ions between which electron transfer is occurring and R is the distance of closest approach. The current can therefore be written as:

$$i = 2eC_{H^+} \int W_{if}(\epsilon_i) n(\epsilon_i) \rho(\epsilon_i) d\epsilon_i, \quad (22)$$

where C_{H^+} is the surface concentration of reactants, $n(\epsilon_i)$ is the Fermi distribution and $\rho(\epsilon_i)$ is the density of states. Introducing the expression for $W_{if}(\epsilon_i)$ in (22), we get:

$$i = 2eC_{H^+} \rho^* \left(\frac{\omega_o}{2} \right) \kappa(n, n') \int \frac{\exp\{-(\epsilon_i - \epsilon_{nn'}^o)^2/4E_s kT\}}{\{\exp[(\epsilon_i - \epsilon_F)/kT] + 1\}} d\epsilon_i, \quad (23)$$

where:

$$\epsilon_{nn'}^0 = \epsilon_F + E_s + (J_f - J_i^0) - e\eta,$$

where ϵ_F is the Fermi energy, and η is the overpotential; κ is the transmission coefficient.

Under the special condition $|e\eta - (J_{fn'} - J_{in}^0)| \ll E_s$, when equation (23) is solved by Laplace's method (i.e., by the steepest descent method for the function of a real variable), it yields⁹ the equation:

$$i = eC_{H^+} \rho^* \omega_0 \kappa(n, n') kT \exp \left[- \frac{E_s}{4kT} - \frac{(J_f - J_i^0)}{2kT} + \frac{e\eta}{2kT} \right], \quad (24)$$

which is of the same form as Tafel's equation.

Thus, the important point is that the well known Tafel relation so widely found to be applicable is obtained from the EF model only when:

$$|e\eta - (J_f - J_i^0)| \ll E_s.$$

This is a very restrictive condition. In fact, the region of overpotential where the above condition holds is about 0.4v., whereas, experimentally, the linearity continues over a range of >1v.

IV. COMPARISON WITH EXPERIMENT

1. Relation between k_{het} and k_{hom}

An argument which has been used to support the continuum electrostatic theory¹² is that the rate constant for the heterogeneous reaction can be predicted from the rate constant for the homogeneous reaction.

The prediction is:

$$\left(\frac{k_{\text{hom}}}{z_{\text{hom}}} \right) = \left(\frac{k_{\text{het}}}{z_{\text{het}}} \right)^{\frac{1}{2}},$$

where k_{hom} and k_{het} are the rate constants for the exchange reaction in solution (e.g., $\text{Fe}^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{Fe}^{3+}$) and at an electrode (e.g., $\text{Fe}^{3+} + e(\text{M}) \rightarrow \text{Fe}^{2+}$). However, it is simple to demonstrate¹³ that such a relation is expected independently of model, so long as the mechanism of both homogeneous and heterogeneous reactions is the same.

2. Predictions of the Free Energies of Activation from a Continuum Electrostatic Theory

From (23), the free energy of activation is:

$$\Delta F_{\text{calc}}^* = \frac{\left[(J_f - J_i) + E_s \right]^2}{4E_s kT},$$

E_s being defined as in equation (21).

ΔF_{calc}^* values were computed for 52 reactions, including both the electron exchange (e.g., $\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+}$) and usual electron transfer (e.g., $\text{Fe}^{2+} + \text{C}_e^{4+} \rightarrow \text{Fe}^{3+} + \text{C}_e^{3+}$) reactions. They were made for various ligands, as well.

The ΔF_{calc}^* is plotted against the experimental ΔF^* value in Fig. 1. There is no co-relation between the prediction of the electrostatic fluctuation approach with experiment.

For ions of radius about 3\AA , water molecules no longer orient around the ion, or remain attached to it for significant times. The continuum viewpoint (which discounts the effects of such an oriented layer) might then be more applicable. Hence, a plot of $\frac{\Delta F_{\text{calc}}^{O^*}}{\Delta F_{\text{expt}}^{O^*}}$ would be expected to tend to unity with increasing radius. The test (Fig. II) does not support the applicability of EF.

3. Variation of β with overpotential and the Tafel relationship from both approaches

In Figure III the transfer coefficient, calculated according to the electrostatic fluctuation theory, is seen to vary linearly with overpotential. Using these values of the transfer coefficients for $E_s = 2\text{ev}$, the predicted Tafel line is shown in Fig. III. There is no linear region, in marked variance with the predictions of the models in electrode kinetics.

In the collisional activation model²⁴ β is:

$$\beta_c = \frac{1}{2} - \frac{1}{2ax_0} \frac{1 - \{(\langle \Delta H_1^{O^*} \rangle - (1 - \beta)F\eta)/D_1\}^{1/2}}{1 - \{(\langle \Delta H_1^{O^*} \rangle - A_0 + F\eta)\}^{1/2}} \quad (26)$$

Here, β is at first constant, but varies at high overpotential. The variation is shown in Fig. III. The agreement with experiment is reasonable.

V. DISCUSSION

The fact that the current-potential relation obtained from the EF model arises from the parabolic nature of the potential-energy profile assumed in that model. Sufficiently small perturbations in libratory oscillations of the solvent molecules, far away from the ion, must be harmonic, so that introduction of anharmonicity to the present model is not acceptable.

Polaron theory in solids, where a system of interacting oscillators are coupled to one another, has postulated fluctuations of the type discussed. In a liquid without appreciable periodicity, the applicability of the polaron theory is more difficult to accept¹⁴. Damping of the wave would have to be introduced and there is no way at present of discovering these factors.

The rotation-vibrational energy levels in H_3O^+ ion are not far apart compared with the observational significance in electrode kinetics (1mev). As a consequence of the frequent collisions between the solvation ion and the surrounding water molecules, they are smoothed out. The continuous relation observed in electrochemical kinetics between rate and overpotential could not be obtained if they were. The opinion that thermal activation would produce a structured Tafel line was a principal reason for suggesting a model basically different from collisional activation. According to Falk and Giguere¹⁵, for liquid H_2O there is a continuum of energy states from 60 to 3444 cm^{-1} (cf. O'Ferrall et al¹⁶). Thus, classical (continuous) modes of heat transfer are available in water and, in particular, aq. H_3O^+ . The appreciable partial molar heat capacity (C_p) at room temperature for H_3O^+ , indicates a range of frequencies giving classical C_p contributions in this molecule (and hence in H_3O^+), and

provides compelling evidence for the above conclusions. In the gas phase, translational energy is converted into vibrational energy (after collision), and it is reasonable to assume that the same process occurs in liquid water. The translational energy of free waters obeys a Boltzman distribution of energy and is in equilibrium with the H_3O^+ ion in solution. The vibration-rotational energy levels of the H_3O^+ ion will also have a Boltzman distribution (at least up to a certain energy level. There are¹⁷ sufficient O-H bonds in an activated state to sustain the reaction over the range of rates observed for electrode reactions on various metals.

If the linear spheres of the reactant and product are different, there must be inner sphere activation to satisfy the Franck-Condon restriction of the electron transfer process¹⁸. Thus, the reactant and product activated state must be in resonance and identical. If the inner sphere is different, activation must occur in it before the right activated state can be obtained. The explicit omission of considerations of the inner sphere⁹ in EF implies that the inner sphere for reactant and product have the same energy, without activation. Applied to $\text{H}_3\text{O}^+ + e_{\text{M}} \rightarrow \text{H}_{\text{ads}}$, such a concept is unreasonable and a model based on it⁹ unacceptable for such reactions.

The Born-Landau Hamiltonian arises when the electronic adiabatic approximation is used to treat the problem of an electron trapped in a polar solvent. This approximation can be applied if the binding energy of the trapped electron is smaller than the binding energy of the medium electrons. It is a satisfactory approximation in a polar crystal where the binding energy of the trapped electron has been shown (Markham and

Seitz¹⁹ and Frohlich²⁰) to be of the order of 0.1 ev, much less than the binding energy of the medium electrons. With polar liquids, however, the situation is different. The binding energy of the medium electrons (4-5 ev) is of the same order of magnitude as the binding energy of the trapped electrons (1-2 ev); the electronic adiabatic approximation thus becomes invalid. To calculate the binding energy of electrons in polar liquids, Jortner²¹ suggests that the trapped electron and the medium electron should be treated on an equal basis and uses the independent particle treatment, treated in terms of self-consistent field theory. The difference between the results of this approach and those obtained with the electronic adiabatic approximation, is due to the fact that in the self-consistent field scheme, the electronic polarisation does contribute to the binding energy of the electrons. Thus, the potential becomes of the form $\frac{e^2}{2r} \left(1 - \frac{1}{\epsilon_s} \right)$ instead of the $\frac{e^2}{2r} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_{stat}} \right)$ involved in the expression derived from the electronic adiabatic approximation. The reorganisational energy would no longer be given in terms of the Born-Landau equation. It would correspondingly, not be given by the time-average Born energy, but by an equation for the change in the orientation energy on ejection of a charge into a polar dielectric.

Hitherto, we have discussed the different degree of agreement with experiment achieved between the two models, and also some fundamental difficulties both in the origin of the fluctuational model and its use of the Born-Landau equation. However, we have not discussed the most important difference between the two approaches. This is the nature of the activation process. The thermal view considers that vibrational

excitation, due to collisions between the ion and solvent very near to the electrode creates the activated state necessary for electron transfer. It does not, thus, differ from well-known concepts in reaction kinetics. The electrostatic fluctuation assumes that an electrostatic fluctuation in the ion-solvent interaction is the origin of the activation. Let us calculate which mode of activation gives the higher probability of obtaining activated states of certain values.

Consider a situation where an ion (including the diameter of a water molecule in the inner solvation sheath) is r_i and a charge of $+e$ is surrounded by N water dipoles. For non-interacting dipoles, the probability of the dipole having an angle between θ and $\theta + d\theta$ at a distance between R and $R + dR$ from the ion, is:

$$P_i = \frac{dN(\theta, R)}{N} = \frac{\frac{3}{2r_\omega^3} \exp\left(\frac{e\mu\cos\theta}{\epsilon_s R^2 kT}\right) R^2 dR \cdot \sin\theta d\theta}{\int_0^\pi \int_{r_i}^\infty \frac{3}{2r_\omega^3} \exp\left(\frac{e\mu\cos\theta}{\epsilon_s R^2 kT}\right) R^2 dR \cdot \sin\theta d\theta} \quad (27)$$

Equation (27) is obtained for non-interacting dipoles. There are of course very strong interactions in a polar liquid such as water.

Following Kirkwood²², let us represent the case in water also as a system of non-interacting dipoles having the effective dipole moment μ_{eff} given as:

$$\begin{aligned} \mu_{\text{eff}} &= \mu + g(\overline{\mu\cos\gamma}) \\ &= \mu(1 + g \overline{\cos\gamma}) , \end{aligned}$$

where g is the number of neighbour water molecules around any water molecule, and $\overline{\cos\gamma}$ is the average cosines of the angles between dipole moments of the central molecule and those of its neighbours. In evaluating $\overline{g\cos\gamma}$, Kirkwood²² considered the nearest neighbours and Pople²³ extended Kirkwood's²² treatment and considered the contribution of both first and second layers of water molecules and obtained $\mu_{\text{eff}} = 1.53$ as the effective dipole moment of water in water. Therefore, in liquid water we consider a system of N -non interacting dipoles, however with an effective moment different from that in the vapour phase.

On this basis, eqn. (27) becomes:

$$P_i = \frac{\int_0^{\infty} \int_0^{\pi} \frac{3}{2r_{\omega}^3} \exp\left(\frac{e\mu_{\text{eff}}\cos\theta}{\epsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta}{\int_0^{\infty} \int_0^{\pi} \frac{3}{2r_{\omega}^3} \exp\left(\frac{e\mu_{\text{eff}}\cos\theta}{\epsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta} \quad (28)$$

The average value of the interaction energy between the ion and the dipole can then be written as:

$$[E] = \frac{\int_0^{\infty} \int_0^{\pi} \frac{3}{2r_{\omega}^3} \left(\frac{e\mu_{\text{eff}}\cos\theta}{\epsilon_s R^2}\right) R^2 dR \exp\left(\frac{e\mu_{\text{eff}}\cos\theta}{\epsilon_s R^2 kT}\right) \sin\theta d\theta}{\int_0^{\infty} \int_0^{\pi} \frac{3}{2r_{\omega}^3} \exp\left(\frac{e\mu_{\text{eff}}\cos\theta}{\epsilon_s R^2 kT}\right) R^2 dR \sin\theta d\theta} \quad (29)$$

It has been shown that¹⁷ the integrals can be evaluated to give:

$$[E] = -\frac{1}{N} \cdot \frac{e^2 \mu_{\text{eff}}^2}{\epsilon_s r_{\omega}^3 kT} \quad (30)$$

The total interaction energy is then:

$$[u] = N[E] = - \frac{e^2 \mu_{\text{eff}}^2}{\epsilon_s^2 r_{\omega}^3 r_i kT} \quad (31)$$

Following a similar procedure, we can evaluate the average square of the energy. This is:*

$$[u^2] = \frac{e^2 \mu_{\text{eff}}^2}{\epsilon_s^2 r_{\omega}^3 r_i} \quad (32)$$

The mean square deviation then is given as:

$$\sigma^2 = [u^2] - [u]^2 \quad (33)$$

Numerical evaluation of σ^2 shows¹⁷ that it is very much smaller than $[u]^2$. Thus, we can use the Gaussian distribution to evaluate the possibility of fluctuation, i.e.,

$$P_{\text{H}_2\text{O}^+} = \frac{1}{(2\pi)^{\frac{1}{2}} \sigma} \exp \left(- \frac{(u - [u])^2}{2\sigma^2} \right) \quad (34)$$

For the proton-discharge reaction, a typical measured activation energy at the reversible potential is 20kcal/mole. Thus, we need a fluctuation of $(u - [u]) = 20\text{kcal/mole} = 1.39 \times 10^{-12}$ ergs/molecule. Thus, using equation (34), $P_{\text{H}_2\text{O}^+}$ comes out to be $\approx 10^{-41}$.

The corresponding probability of the thermal activation can be obtained from the Boltzman distribution and for the O-H⁺ bond and the

* The value of the dielectric constant to be used in these expressions is that for a time average evaluation, i.e., 80.

activation energy of 20kcal/mole. It is 10^{-15} ¹⁷. Hence, the CA approach gives a far higher probability of creating an electric state suitable for electron transfer at an electrode than does the continuum electrostatic approach.

So far, we have estimated the probabilities at the reversible potential. However, it is important to estimate how these probabilities vary as the potential changes. For the hydrogen evolution reaction, the activation energy at any overpotential is given as:

$$\Delta H^\ddagger = (\Delta H^\ddagger)_{\eta = 0} - \beta \eta F.$$

Thus, the variation of the activation energy with overpotential is known. We can estimate the change of probability with potential using a Boltzman distribution and the fluctuational probability using a Gaussian distribution. The results are tabulated in Table I. The ratio of the two probabilities are plotted in Fig. V. The conclusion is very clear that in most of the experimentally accessible overpotential, the thermal probability is much larger than the fluctuational one.

Thus, the approach arose as a reaction to some misunderstanding of the distance between levels in the vibration-rotation spectra of H_3O^+ in solution. The acceptor states in H_3O^+ arising from the normal Boltzman distribution outweighs the fluctuational probability over much of the range of experimentally obtainable overpotentials, at least for hydrogen evolution.

TABLE I

| η in volts | ΔH^* in kcals/mole | Probability Thermal | Probability Fluctuational | Probability ratio (T/F) | log (T/F) |
|-----------------|----------------------------|---------------------|---------------------------|-------------------------|-----------|
| 0 | 20 | 10^{-14} | 10^{-42} | 10^{28} | 28 |
| 0.2 | 17.7 | $10^{-12.4}$ | $10^{-32.8}$ | 10^{20} | 20 |
| 0.4 | 15.4 | 10^{-11} | 10^{-25} | 10^{14} | 14 |
| 0.6 | 13.1 | $10^{-9.5}$ | $10^{-17.8}$ | $10^{8.3}$ | 8.3 |
| 0.8 | 10.8 | $10^{-8.1}$ | $10^{-12.1}$ | $10^{4.3}$ | 4.3 |
| 1.0 | 8.5 | $10^{-6.7}$ | $10^{-7.6}$ | $10^{1.4}$ | 1.4 |
| 1.2 | 6.2 | $10^{-4.5}$ | $10^{-4.2}$ | $10^{0.2}$ | 0.2 |
| 1.4 | 3.9 | $10^{-3.0}$ | $10^{-1.68}$ | $10^{-0.9}$ | -0.9 |
| 1.6 | 1.4 | $10^{-0.9}$ | $10^{-0.4}$ | $10^{-0.5}$ | -0.5 |

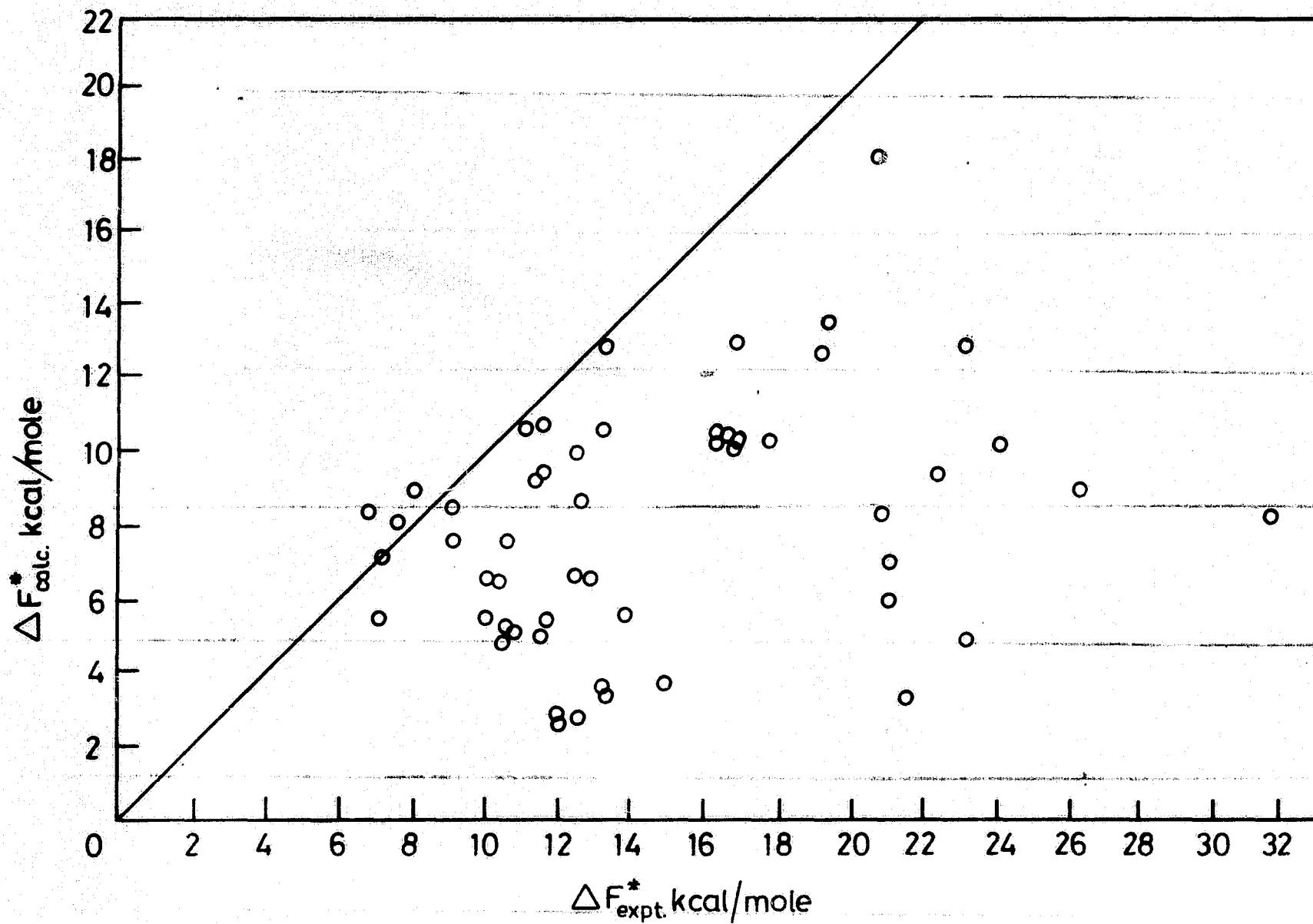
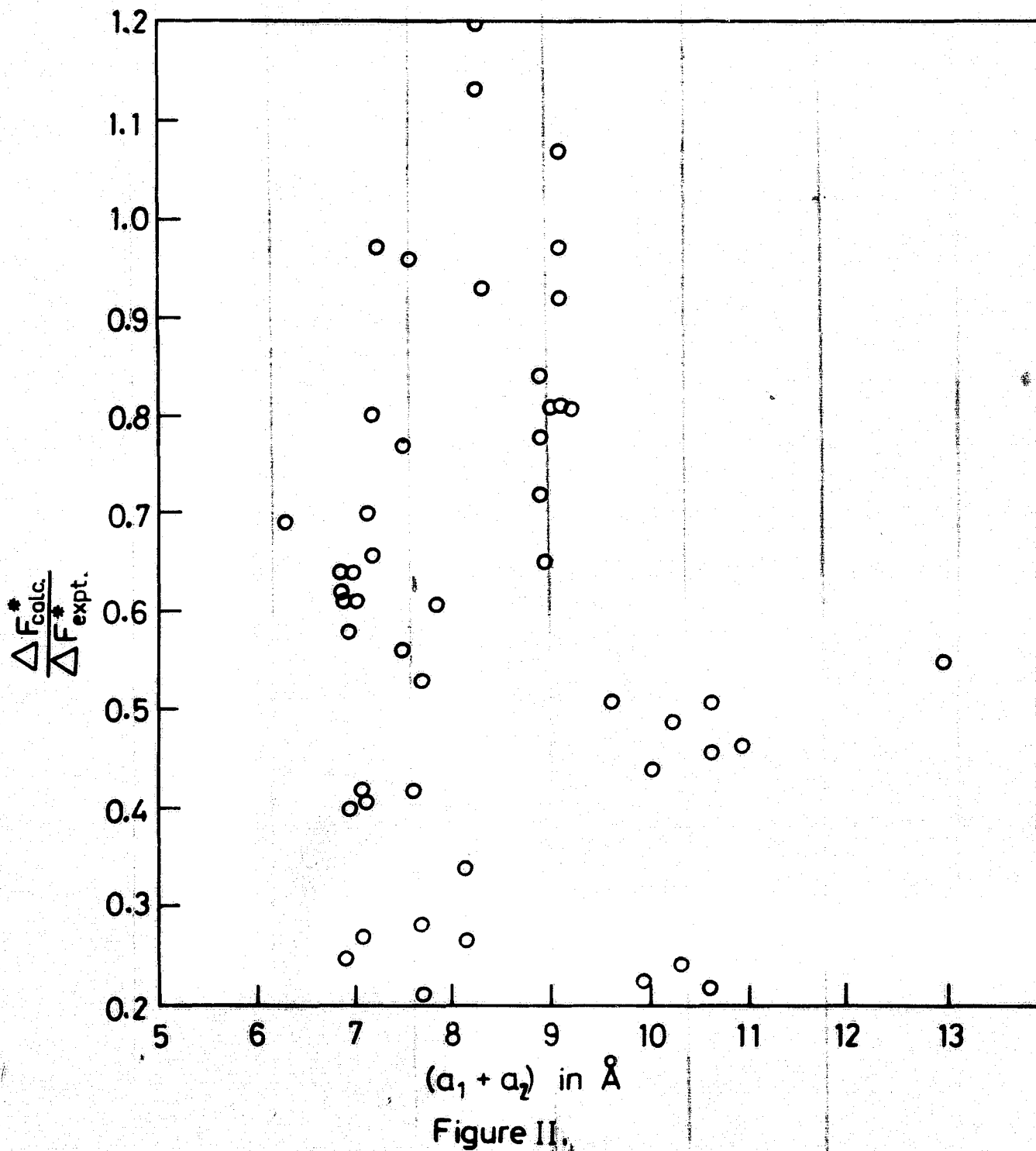


Figure I.



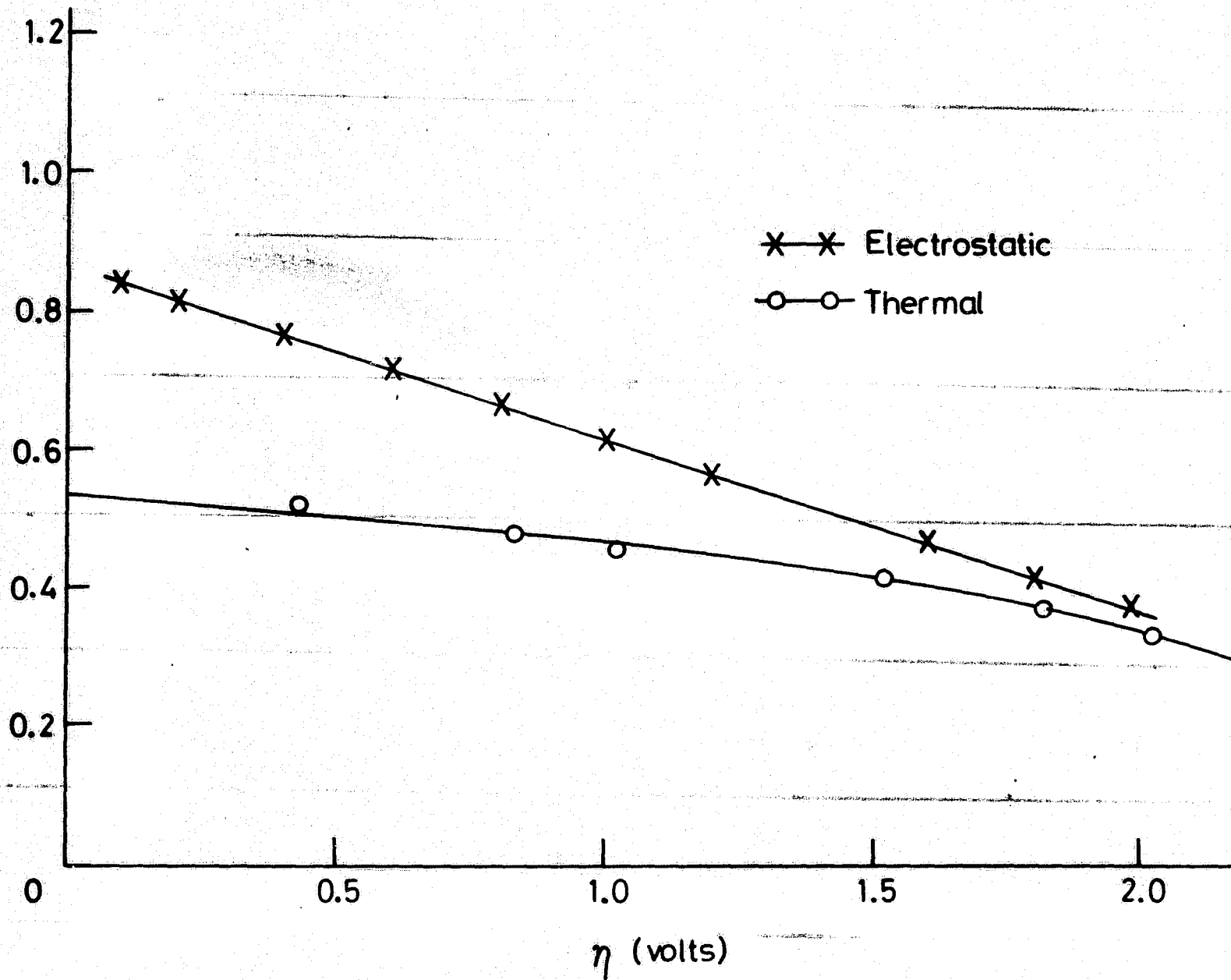


Figure III.

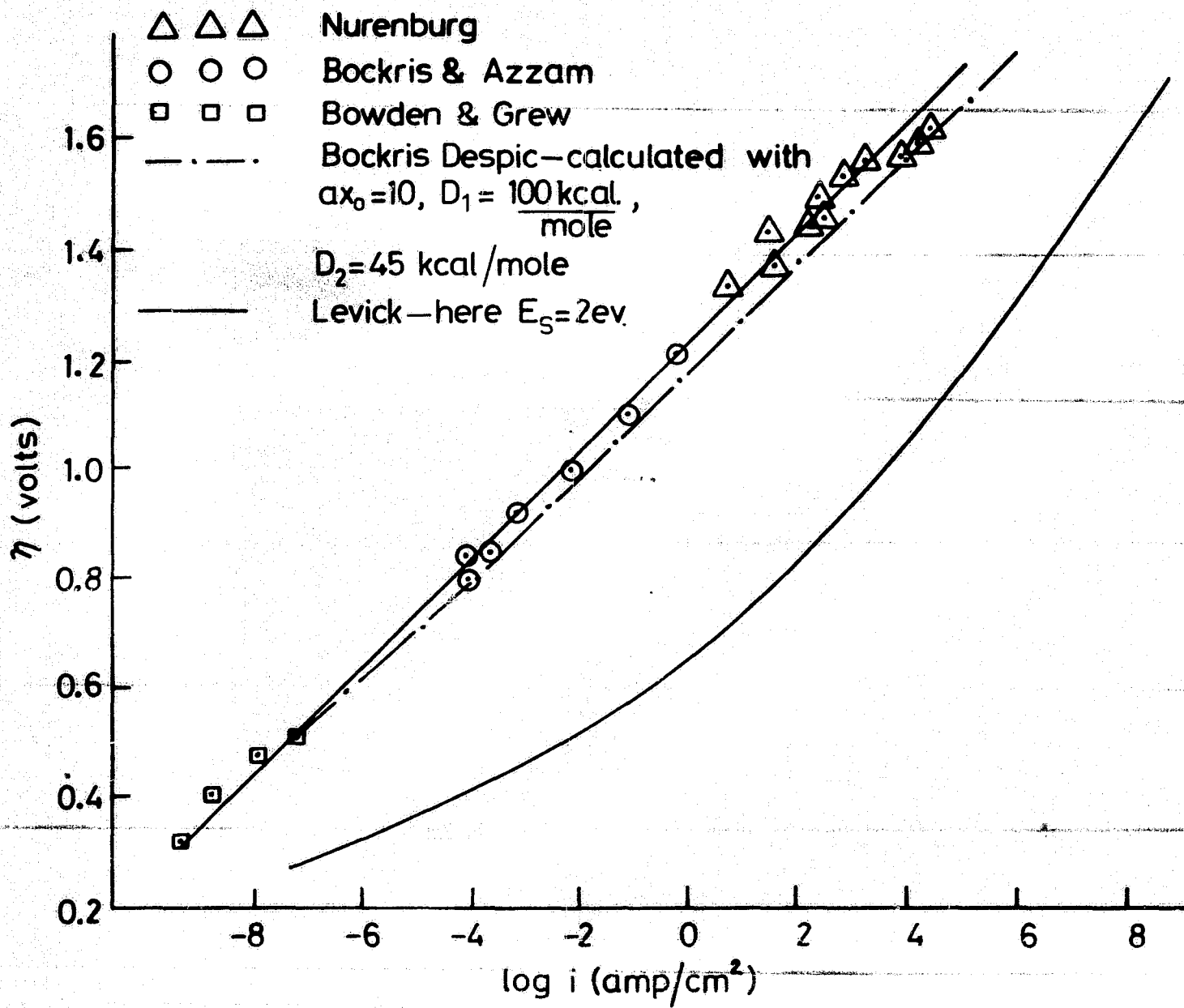


Figure IV.

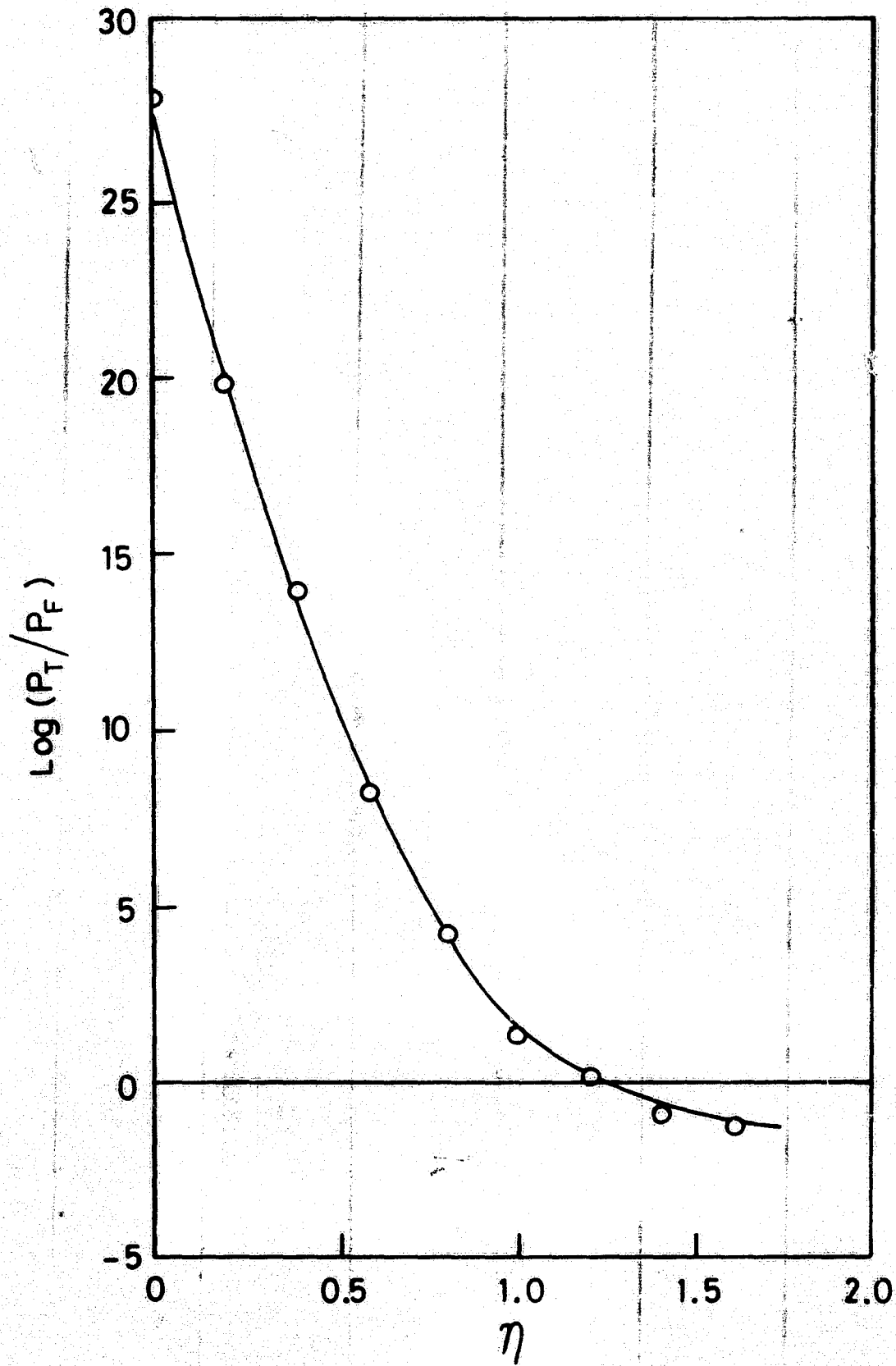


Figure V.

ANNOTATIONS FOR FIGURES

Figure I. The free energy of activation for redox reactions in solution. $\Delta F_{\text{exptl}}^{O*}$ represents the value obtained by equating the experimental rate of $Z \exp\left(-\frac{\Delta F^{O*}}{RT}\right)$, where Z is the calculated bimolecular collision number; $\Delta F_{\text{theoretical}}^{O*}$ is the value obtained from the electrostatic solvent fluctuation viewpoint. There is no correlation.

Figure II. $\frac{\Delta F_{\text{theoret}}^{O*}}{\Delta F_{\text{exptl}}^{O*}}$ as a function of the sum of the radii of the ions. The value does not tend to unity at high radii.

Figure III. β as a function of potential, electrostatic and thermal. That calculated on the electrostatic model with a reorganisation energy of 2ev varies much more over the range 0-1v overpotential than does that calculated from the electrostatic view. Experimentally, the coefficient is nearly constant with potential at over at least 0.5 volts.

Figure IV. The experimental Tafel line for overpotential as a function of $\log i$ in the system: $\text{H}_3\text{O}^+ + e \rightarrow \frac{1}{2} \text{H}_2$ (Points). Broken lines: thermal model. Continuous line: electrostatic fluctuation theory.

Figure V. The relative probability of the activation of protons into states above the ground state by amounts varying from lev to 0. P_T is the probability arising from the theory in which there is equilibrium between the heat sink and the surrounding solvent. P_F is the probability calculated on a fluctuation of the electrostatic energy of the ion.

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MAJOR POINTS FROM SEN'S WORK

1. The relation of friction to potential when the two interfaces are metal-solution, can be interpreted in terms of the repulsion of two Gouy layers.
2. The BDM isotherm allows predictions of a capacitance minimum. It is not inconsistent with thermodynamic reasoning. The polarizability term in the double layer equations may become important at high enough fields.
3. The polaron theory of electrode processes is inconsistent with line broadening in solution.
4. The polaron theory of electrode processes is not consistent with the trend of electrochemical facts about proton transfer.
5. The polaron theory is not able to give the Tafel line.
6. The limits of the Gamow approximation for the probability of transfer are given.
7. The Gurnean and Weissian approaches to electrode kinetic formulations are given.
8. BEBO gives good results for proton transfer.

C-3