ENERGY CHANGES IN ELECTROCHEMICAL PROCESSES - THE ELECTRODYNAMIC MODEL AND THE THERMOELECTRODE

by

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ABSTRACT

This work is devoted to the analytical and experimental study of energy changes occurring at the electrodes during electrochemical reactions. The existing literature is critically evaluated to demonstrate the non-isothermal character of electrode processes. Based on the dynamic interpretation of potential energy functions of interacting species, the electrodynamic model is proposed. Recognizing the existence of the phenomena of excess energy and anodic cooling leads to the development of the thermoelectrode -- a novel instrument to experimentally measure these quantities. Experimental investigations on transition metals is undertaken to substantiate the validity of the model. The findings are thought to be relevant to the industrial practice of metal electrowinning and refining.

CHAPTER I. INTRODUCTION

A. SYNOPSIS

There cannot be a more appropriate way of offering reasons for the need of undertaking this investigation than to quote, with minor editing, the last paper[1] written by the late Prof. R. Piontelli of the Politecnico di Milano, for the Cleveland, Ohio,Fall Meeting of The Electrochemical Society, during October 3-7, 1971.

"General Considerations on Electrocrystallization

Roberto Piontelli, Politecnico di Milano, Italy

> Our present knowledge and understanding about electrocrystallization are very poor, not only from the theoretical point of view, but also as regarded to sound phenomenology. Among all the unsolved problems and the inadequately explored field, it seems that the following ones require particular consideration:
>
> 1) Analogies and differences between electrocrystallization and other kinds of crystal-growth processes. The problem concerning the definition and determination of the over-or under-saturation conditions and other similar subjects are [*only*] briefly discussed [*in the literature*].
>
> 2) Influence of the following factors on electrocrystallization kinetics and on the structural characteristics of the deposit:
>
> α) nature of the deposited metal;
> β) nature, structure, crystallographic orientation, defects, surface conditions, etc. of the substrate;
> γ) bath nature and composition (solvent, anion, pH, additives);
> δ) other work conditions (temperature, electric supply characteristics, etc.).

It is often thought that the properties responsible for the plated metal performance are the herebelow listed ones:

a) electron extraction work;
b) zero charge point;
c) surface inhibition or passivation.

[*Property*] (a) can be correlated with more directly effective properties; (b) is important in considering the influence of (γ); (c) is sometimes very effective, although it does not allow any general explanation of (α). The electrode processes are heterogeneous chemical reactions whose kinetic trends and structural results are mainly determined by the peculiarities of the involved fields of forces, and by the distribution of the reacting species among the available states. Following these imperative lines of reasoning, any satisfactory explanation of the questions (α) to (γ) is a very distant goal however.

3) Differences between the factors involved in the macro-throwing power and those determining the distribution of the nucleation and the growth-rate anisotropy at the microscopic or submicroscopic scale.

4) Adhesion of the deposits to the substrate. This problem is closely linked with (2β), (3), (7α).

5) α) Hydrogen interference in the electrocrystallization;
   β) Anticorrelation between the overvoltages concerning the hydrogen ions on one hand and the metal ions on the other hand. Any acceptable interpretation of this rather widely respected empirical rule would constitute an important progress for (2α).

6) Stress in electrodeposits. In some particular cases (like the ones concerning the occlusion of: hydrogen; anions, colloidal matter) the sources of stresses are considered to be qualitatively understood. On the whole, however, it seems that the problem requires a supplementary investigation.

7) Alloy formation.

α) The points (2) and (4) are linked with the problem relevant to the alloy formation between the substrate and the deposits. Examples are given and interdipendences with allied topics are recalled [*in the literature*].
β) The theory of alloy formation by co-deposition is still largely unsatisfactory.

8) Limit structures.

α) The formation of powdery or similar deposits is usually considered to be a direct consequence of the 'limit-current' conditions. The influence of the nature of deposited metal, bath, etc., suggests the need of a more complete explanation (correlation with (3)).

β) The dendrite formation too, is inadequately understood. The way towards real progress in all these fields (as well as in many others we omitted here) at present appears to be very hard and long, not only from the theoretical point of view, but mainly owing to the need for more experimental data, obtained under properly selected and strictly controlled conditions."

The author of this thesis would like to think that he has in some small way contributed towards these goals through the Electrodynamic Model which he has proposed and the Thermoelectrode which has been developed.

B. STATEMENT OF THE PROBLEM

The established methods of electrochemical kinetics treat the electrode reactions as isothermal processes. The scope of this thesis is to provide proof that a temperature profile exists at the electrode/electrolyte interphase, and therefore that electrochemical reaction must be treated as non-isothermal processes.

This work is mainly concerned with phenomena that affect the physico-chemical characteristics of the products of electrode processes as listed in the Synopsis.

The principal reason why the electrode reactions in electrochemical processes are not sufficiently understood is the type of approach almost universally used to study them. Models based on mechanisms apparently suitable for describing heterogeneous chemical kinetics of isothermal, closed, thermodynamic systems, with superimposition of an externally applied electric field, are used to describe electrode processes. Further, the nature and behavior of variables are carefully chosen so that although they are compatible with fundamental laws, they are not necessarily the best choice for electrochemical systems.

Fig. I,1 represents the curve for the activation energy for electrode processes as illustrated in most textbooks on electrochemistry. The numerical values of the energies as a function of distance is seldom mentioned, nor is the distance

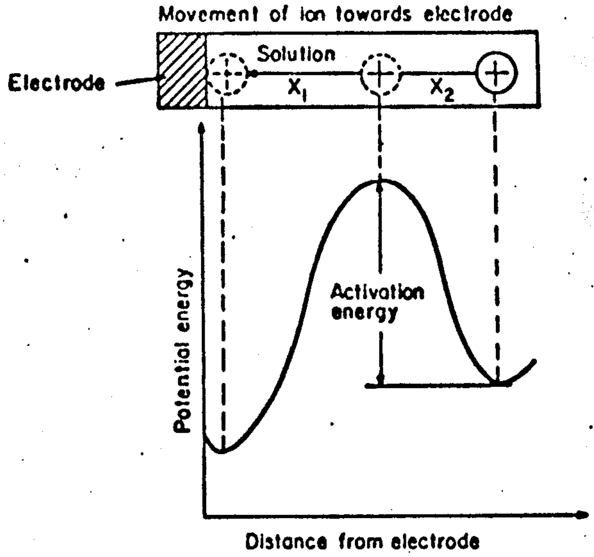

Fig. 8.17. Construction of a potential-energy–distance profile by consideration of the potential-energy changes produced by varying x_1 and x_2.

Fig. I,1 - Reproduced from Bockris and Reddy[2].

scale itself given. Moreover, although it would be very useful to know the contributions to this free energy change, that is, the changes in entropy and enthalpy, this information is also not given.

To understand the activation process it is necessary to know the origin and the source of the energy. In particular -- how and in what manner is the energy actually increased? Also, why are only some species activated and which species are affected thus? Furthermore, if some species is activated, how does de-activation occur? Since the energy balance must be observed, where does the de-activation energy go? From the shape of the curve one is led to believe that the de-activation starts before the species is physically at the electrode surface -- would this mean that the electron transfer takes place away from the metal surface? If this is the case, at exactly what distance from the surface? In short, the curve shown in Fig. I,1 has little meaning unless the above questions are answered.

It is the author's contention that electrode reactions in electrochemical systems must be considered as an individual category with all the special characteristics it embodies. Live electrode processes take place in open, non-isothermal, far-from-equilibrium, thermodynamic systems. The only way of gaining an understanding, is to study them as such; accepting them as they are, instead of assuming unnatural, arbitrary behaviors. The mechanism should be qualitatively defined in detail, such that the physical concepts are clear, then we can impose on the system general expressions to describe it. Instead we often read that one is not going to use a qualitatively clear model representing the reality because the analytical treatment will become too complicated. Thus, many authors in the literature have concentrated their efforts in producing a large number of fine works in equilibrium electrochemistry -- which will be referred to as Thermostatics -- that are of little use in the investigation of live electrode processes, in which, truly, Thermodynamics is involved.

In the light of the above considerations, a study of the mechanisms of electrode processes will be conducted in order to obtain an accurate description of the energy changes occurring at the electrode/electrolyte interphase. A model representing a simplified electrode reaction will be proposed and an instrument to measure the energy changes will be developed, in order to reduce the theory to numerically usable results.

Electrode/electrolyte systems which form semiconducting layers at the interphase are beyond the scope of this investigation. However, some of the works in this field will be mentioned because their informational content is pertinent to this work. Further, this work is not concerned in studying how irregularities, dendrites and whiskers grow from a nucleation point on the metal electrode surface. Instead, one of the primary aims is to explain how the nucleation point is formed in the first place, and to comprehensively account for the variety of deposit morphologies which range from specularly flat to powder.

Finally, it will be demonstrated that many of the presently insufficiently understood electrode process phenomena may then be explained very simply when the assumption of isothermal behavior is abandoned.

C. ORGANIZATION OF THE WORK

This investigation is organized into eight chapters. In Chapter II an extensive literature survey is summarized and a critical evaluation of current methods of electrode kinetics is presented in Chapter III. The novel electrodynamic approach of this thesis is developed in Chapter IV and the model is proposed in Chapter V. Chapter VI presents a reduction of the model to numerically usable results. The evolutionary development of the thermoelectrode and its use in the experimental part of this investigation are reported in Chapter VII. Finally, the concluding remarks in Chapter VIII provide the relevance of this work to practical electrode processes, along with guidance for future work.

CHAPTER II. LITERATURE SURVEY

A. INTRODUCTION

This survey is by no means complete nor exhaustive, since the number of works falling into the general definition of electrochemical kinetics and available in the literature is very large. Only the authors who have been responsible for originating the various treatments, lines and schools of thought, and/or have presented comprehensive reviews have been included. The author's primary intent in doing this survey was, that by reviewing the published works, he would be able to refine his own ideas on electrochemical kinetics, and thereby produce constructive criticisms pointing to the need for developing and building the electrodynamic model.

This attitude is best qualified by one of Henry Eyring's famous statements -- "Why should we be concerned with the mistakes of others? Science progresses with the cooperation of many scientists".

B. HISTORICAL REVIEW

Bockris[2] offers what is probably the best historical review of electrochemical kinetics. His "Great Nernstian Hiatus" of the potential-centric treatment of electrochemical reactions gives the evolutionary explanations of the present state of the theory. It is worthwhile mentioning that

Bockris is regarded as the most dynamic, polyvalent and incisive scientists in the overall field of electrochemistry. In fact his work has been the single most consulted source of information during the development of this investigation.

C. CLASSICAL THERMODYNAMIC APPROACH

To date only a few, simple electrochemical systems have been fully treated with thermodynamic methods, and works of Guggenheim[3,4] on charged systems without polarization and on non-conducive homogeneous, polarized dielectrics, may serve as examples of the degree of development. At the beginning of his last work, he offered an enlightening judgment -- "...this particular subject has a history which is especially interesting, inaccessible and, so far as it is accessible, inaccurate...".

Hill's work[5,6,7] on thermodynamics of small systems represent the maximum result that can be obtained in the effort of using macroscopic thermodynamics with correction factors to account for the dimensional effects in the description of limiting small macroscopic systems. Difficulties arise from the definition of limiting small macroscopic systems, and in the numerical calculation of the correction factors.

Sato[8] has used this approach to derive the stress equation for anodic films, limited to the effects of interfacial tension and electrostriction pressure only.

D. LOCAL THERMODYNAMIC APPROACH

Sanfeld's work[9] shows to what extent irreversible thermodynamics can be used to describe the properties of charged interfaces and in particular those of the electric double layers. It is based on the treatment of local formulation of thermodynamics developed by the Belgian school of thermodynamics[10]. Prigogine's foreword of Sanfeld's work clearly defines the limits of this approach --

> "It is clear that thermodynamics alone is not sufficient to give a theoretical interpretation of the present experimental information. But whatever the ideal mixture of thermodynamics and molecular physics may be in each specific case, it is important to be fully aware of the exact range of the thermodynamic methods."

Sanfeld opens his very carefully presented book[9] (the glossary of symbols is ten pages long) with this statement:

> "Technological results in these fields [*electrochemistry and related*] are beyond comparison with theoretical progression. This arises from the lack of a coherent theoretical formulation, even for equilibrium systems."

Sanfeld implicitly comments on Hill's type of thermodynamic approach by showing why it is wrong to correct the equation of distribution of matter in a field by the arbitrary allowance for volume, polarization and pressure effects, which result in expressions having hybrid internal structure. He feels it is very difficult to explain microscopic regions in terms of macroscopic variables such as polarization vector and pressure. While in agreement with the above views, Sanfeld's criticism that the region nearest to the interphase should not be considered a peculiar medium, very different from more distant regions, can not be accepted. As it will be seen in this thesis, the electron surface is the location of a discontinuity. Clearly Sanfeld is driven on that line of thought by the major assumption of any thermodynamic method -- that all systems studied are continuum. Sanfeld offers what is probably the clearest proof of the failure of classical global thermodynamics in the treatment of electrode processes. He points out that electrostatic energy cannot be decomposed into parts localized in homogeneous phases. In electrochemical systems, however, where charges are unequally distributed and a macroscopic field tends to displace charged particles, an important part of the free energy is localized in the interfacial layers. Thus, it is in this region that the field differs from zero, and therefore, where its entropy effect and electrostatic energy are localized. Sanfeld shows that it is hypothetically still possible to define a new Helmholtz free electrochemical energy of the interphase region, which do not only depend upon its internal values of temperature, volume and number of molecules, but also depends upon the variables involved in properties of its interfacial layers, the state of which depend on the field created by the neighboring phases. The volume free energy represents only a part of the free energy of the system, and to obtain the total free energy we must add to the previous the excess* free electrochemical energy of the layers.

In concluding, Sanfeld states that classical global thermodynamics does not provide connections between thermodynamic functions (chemical potential) and local variables (temperature, concentration, pressure, electric field) unless (a) the system is in equilibrium, (b) it contains all the charges, and (c) the external electric field energy is considered to exist in an "infinite" medium, is entirely included in the system. Therefore, one is obliged to use local formulations to localize the free energy in each volume element of the system, since electrostatic energy depends on all the charges and this mutual interaction prevents a simple and correct definition of the free energy of one of the phases. Sanfeld presents in detail Prigogine's thermodynamic treatment, and a most important point is the local formulation of the second principle --

> "In every macroscopic region of a system, the entropy production due to irreversible processes is positive."

This definition is much more restrictive than the definition used in classical global thermodynamics for which only the total entropy production for the system as a whole is positive implicitly allowing for the possibility of negative entropy production in some region of the system. As it will be seen

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* Hill's excess quantities relative to macroscopic.

in this thesis, this strict local definition of thermodynamic functions is important for the electrodynamic model formulation. But even with local formulation the behavior of different unit volumes cannot be regarded as completely independent; the entropy flow provides the relationship between regions. Thus, Sanfeld, after extensive development of his treatment is obliged to conclude by saying --

> "Thermodynamics of irreversible processes, in its present form, is only valid in a region near equilibrium. If we are very far from equilibrium, we must use statistical methods and thermodynamic methods are no longer of any use." [11]

Nevertheless, Sanfeld's work is probably one of the best treatments developed in detail without many of the simplifying assumptions so frequently made in the field. His assumptions are clearly stated and their relative importance stressed.

E. ELECTROCHEMICAL THERMODYNAMICS

Van Rysselberghe is one of the few electrochemists fully familiar with thermodynamics of irreversible processes[12]. These comments are mostly based on his 1966 work[13] in which his views are comprehensively expressed. Often, in the course of his work, he complains that little systematic use of thermodynamics has been made in the various areas of electrochemistry concerned with non-zero currents, and that the premature introduction of all the details of an assumed picture of the electrochemical double layer hinders the progress in these areas.

The basic idea of his approach is the concept of "Integrity of the Electrochemical Potential" -- the arbitrary separation of electric and chemical contributions in the electrochemical reacting species, followed by separate treatments of these contributions cannot be allowed. It is unfortunate, however, that after having blamed much of the current literature on electrode kinetics for the a priori introduction of transfer coefficients in certain electric terms, he then goes through the trouble of showing the connections between his Marcelin-DeDonder kinetics and the Absolute Rate Theory.

During the critical evaluations of the assumptions made in his treatment, Van Rysselberghe makes an interesting consideration, suggesting that, in some regions of the interphase between the bulk of the metal and the bulk of the solution some thermodynamic quantities may exhibit discontinuities. This is one of the fundamental points upon which the electrodynamic model developed in this thesis has been based.

The only weak aspect of Van Rysselberghe's work is his improper use of the Sign Convention in the confusion of which he became immediately entangled in his first example of galvanic cell study, switching superscripts, changing signs, and justifying it by saying that the numerical value of an ion charge changes its signs depending on whether the reaction occurs as written or in the reverse direction. It would not be improper to point out that this confusion in sign convention is common to the majority of authors, who regard the electrons traveling the electrodic part of the circuit as entities external to the electrochemical system.

Once the above problem is resolved, Van Rysselberghe's work is one of the best treatments of the concept of Electrochemical Affinity. The anodic and cathodic entropy production and the Joule effect are precisely considered.

As noted earlier, Van Rysselberghe does not offer any substantial improvement on the method for determining electrochemical charge transfer coefficient - exchange current density.

Piontelli developed ideas in close agreement with Van Rysselberghe. He did so, independently at first using a similar approach to non-equilibrium electrochemistry on the basis of non-equilibrium thermodynamics. Piontelli later presented Van Rysselberghe's views before the Accademia Nazionale dei Lincei in 1961[14]. This particular paper is enlightening in that it presents the state of the art of Electrochemical Kinetics and translated abstract is given below.

> The usual treatment of electrodic kinetics consists in an intuitive combination of principles and methods of chemical kinetics, with empirical factors introduced to take into account the influence of the electric potential difference between electrode and solution. Qualitative considerations have been developed on the bases of arbitrary traced potential energy curves, while thermodynamic quantities have been introduced without adequate bases. On such uncertain bases, correlations between overtensions and heat of adsorption of atomic hydrogen on the electrode metal, or the electron extraction work have been sought with only partial success. The transfer coefficient has never had a definition free from ambiguity; while, for the reverse process it has almost always been assumed to be the complementary of the coefficient of the direct process.

Piontelli is the only electrochemist to use concepts close to Prigogines' local thermodynamic formulation[15,16,17]. In a late paper of his[18], he questioned the applicability of macroscopic thermodynamics of heterogeneous equilibria to the investigation of electrodic systems. In fact, while the simplifying set of hypotheses on which the phase rule is based are generally acceptable for chemical equilibria studies, they are apparently invalid for conditions of an electrodic system; as for example, the negligibility of long range fields, surface effects, and the electrical neutrality of the phases involved. Indeed, in electrode processes we have non-uniform distribution of charges and matter.

In the light of these considerations, Piontelli makes a very interesting suggestion to the effect that due to the complexity of such distributions it would be preferable to speak of "interphase region" instead of a double layer as is customary, in which a kinetic equilibrium is established under the influence of the electrical conditions of the phases as a consequence of both exchanges between the phases and of external influence.

Regarding the concept of exchanges between phases, Piontelli offers another very interesting observation, (which is one of the bases of the electrodynamic model) -- in electrode processes we do not have a true exchange of matter between metal electrode and electrolytic solution, but a transfer between these and the interphase region.

Piontelli's analysis of the essential aspects of the condition of kinetic equilibrium can be summarized as follows --

1) the electrical neutrality of the electrode and electrolyte phases must be observed, in order to obtain uniformity in the electrostatic potential, which in turn is necessary for the uniformity of the electrochemical potential of the charge carriers in each of the above two phases;

2) the contribution to the formation of the interphase region comes from constituent species:
   a) in part as electrically neutral species having the characteristics of having an oriented dipole or of being ionically dissociated within this interphase region;
   b) in part as electrically charged species whose loss corresponds for each of the two phases to the loss of charges of the same value but of opposite sign that go to segregate on the "free" boundary of the phases where they contribute to establish the Voltaic field;

3) the establishment of the equilibrium depends solely upon the Galvanic potential, that is the difference between the macroscopic electrostatic potentials inside the electrode and inside the electrolyte, which in turn is a unique function of the variables defining the physico-chemical local state of the two phases.

Piontelli has studied the applicability of the principles of symmetry to electrodic systems[19] to a greater extent than any other electrochemist; Bockris, in using the symmetry factor, did not seem to have stressed any point beyond the geometrical symmetry of the activation energy barrier.

As it has been seen, the previous two authors did not seem to have particularly stressed the role of temperature resulting from heat changes in electrode processes. Among the very few authors who did, Bockris and Srinivasan in their work on fuel cells[20] have pointed out that even in ideally hypothetical cell operation, heating effects will occur when the overall entropy change is negative. They added that these heating effects are very small, if compared to heat associated with combustion engines; but, we must note that (and this is a key concept of the electrodynamic model) these heating effects are also very localized in the small volume element of the interphase. That is to say that the heating effect occurs when the overall enthalpy change is larger than the overall free energy change for the cell reaction, which is the part which is converted into electron potential difference. In the opposite case, when $\Delta G > \Delta H$, we have an apparent efficiency larger than 100%, in terms of Faraday efficiency; this arises from the fact that ΔS is positive, which means that heat must be absorbed from the surroundings otherwise the cell cools; and here again, we must note that the coolest region is the interphase, and this is another key concept of the electrodynamic model.

Bockris and Srinivasan, after having further stressed that it is not true that electrochemical energy conversion takes place completely without temperature change even when working under ideal conditions, examined the various possible locations of the heat changes in an ideal electrochemical energy converter; and their observations are reproduced here below (from page 160-1 of ref. 20) --

> "In most of the existing fuel cells, the heating effects observed within the electrolyte are due to ohmic losses. The rate of heat liberation is given by I^2R_i, where I is the current and R_i the ohmic resistance of the electrolyte. In an ideal electrochemical energy converter this loss is zero, but there is still heat evolved if the entropy change of the cell reaction is negative.

> The heat evolved is numerically equal to TΔS per mole of fuel consumed. Since ΔS is equal to nF(dE/dT), this heat change may be broken up into three components: heat evolved at each of the two metal-solution junctions and the metal-metal [*Peltier*] junction. It is likely that the major contribution to the heat evolved occurs at the two metal-solution interfaces. Thus, the heating effect at the metal-metal junction is small because the potential difference across this junction is equal to the difference in work functions of the two metals and the temperature coefficient of work functions are small.
>
> It must be carefully noted that the above discussion of the relation between the free-energy change of an overall reaction and the potential developed in a cell assumes estrapolation of a real case to an ideal one -- namely, the electrochemical reaction is carried out sufficiently slowly so that it may be regarded as behaving thermodynamically reversibly. Realization of the ideal situation treated above, is equivalent to the case in which an electrochemical energy converter works at an efficiency of 80 to 90 per cent or even greater, but at a negligible rate of doing work, i.e. at a negligible power."

[the following is a footnote in Bockris' and Srinivasan's work immediately following the above text.]

> "The maximum intrinsic ideal efficiency of most fuel cells is in the range of 80-96 per cent at room temperature and not 100 per cent as sometimes stated. Thus, 100 per cent of the free energy change could be recovered as electrical energy in an ideally operating fuel cell, but this free energy change is generally numerically less than the enthalpy change of the reaction. Conversely, in the rare case when $|\Delta G| > |\Delta H|$, the ideally operating fuel cell could produce electrical energy in excess of the enthalpy change of the reaction. The extra energy comes from the heat energy of the surrounding atmosphere."

This is one of the few instances found in the literature where the existence of an electrode excess energy is considered and we will subsequently see the importance of the above observations in the development of the electrodynamic model.

F. EASTMAN NON-ISOTHERMAL THERMODYNAMICS

Eastman's work[165] is regarded by the writer as the most advanced treatment on the energetics of electrochemical processes in spite of the early date (1926-28). His work is based on a very clear insight of the physical meaning of entropy.

In order to follow the train of thought along which Eastman developed his theory, it is regarded as most appropriate to reproduce some of the passages from his published works (of which only four were found), which are most relevant to this investigation, and do not seem to have been given enough stress by recent reviewers -- Agar[121] in 1963 and Wagner[122] in 1972.

In Eastman's first paper[165a] the physical meaning of non-isothermal equilibrium is described as follows --

> "In illustration, the transpiration of a gas through perforations in a wall between a hot and a cold region may be considered. When the mean free path of the molecules is sufficiently large they will pass back and forth through the wall without undergoing collision in the orifice. When the number* of molecules passing in each direction is the same, equilibrium is established. When this condition is fulfilled, a pressure difference on the two sides of the dividing wall is found to exist. But in this state of balance, the molecules passing from the hot to the cold compartment in any given time transfer larger amounts of heat than those passing in the

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* The underline is an editing addition in order to stress the relevance of this reasoning to electrochemical processes in which the number of species passing at the two electrode/ electrolyte interphases is the same in terms of equivalents.

> same time in the reverse direction. The equilibrium therefore, is incomplete. It follows that it cannot be exactly treated thermodynamically (though it obviously may be by kinetic theory). The distinguishing feature of the system in this illustration is that the mechanism of conduction of heat is identical with and inseparable from that of transfer of material between regions."

This type of reasoning is of paramount importance and constitutes the foundation of the electrodynamic model developed in this thesis.

The difference between the system, comprising the substances undergoing the process, and the reservoir, which is defined as the environment in which the process occurs, each associated with its own value of entropy, is another concept of great importance. Eastman did not strongly emphasize this difference in his first paper and this provoked the publication of a note of discussion by Rodebush and a rebuttal by Eastman[165b] in which he states --

> "Some confusion may, however, have been caused by my repeated references to the 'system' and the 'reservoirs', since the two together constitute the larger 'isolated' system (of constant energy) to which the condition for equilibrium was applied."

In the same note, he goes on to reiterate on the difference between non-isothermal and isothermal equilibria --

> "Whereas the latter [*isothermal*] are independent of the process through which equilibrium is achieved, the former [*non-isothermal*] depend entirely upon it. The reason for this is, of course, that by different processes of transfer of the same amount of material, different amounts of heat are moved between the lower and higher temperatures. Different changes in state, when this is considered, are therefore brought about in such processes."

In his first paper[165a], Eastman also describes the mechanism by which heat is transferred from a colder to a warmer region in two cases: (a) during the discussion of the phenomenon of thermal endosmosis occurring between two chambers maintained at different temperatures and separated by a membrane permeable only to the substance considered --

> "If under equilibrium conditions in this system one mole of the substance is transferred from the colder to the warmer compartment, two transfers of heat occur which may be considered separately. The first of these is the loss by the reservoir to the system of a quantity of heat equal to the difference, dH, in molal heat content of the substance in the two compartments. The second effect arises from the fact that in general a heat effect attends the solution of the substance in the membrane at one temperature and its withdrawal at another, the result of which is a transfer of heat between the reservoirs at different temperatures."

and (b) during the determination of the entropy change due to osmotic temperature*.

At this point of his first paper[165a], in discussing about the Soret effect**, Eastman anticipated the key concepts of his theory --

> "Consider the transfer (spontaneously occurring under conditions very close to equilibrium) of a

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*The definition presented by Eastman[161a] is the following: "The decrease in activity of a solvent caused by the presence of a solute might be compensated by an increase in temperature as well as by an increase in pressure (as in the usual osmotic equilibrium) [...]. The temperature difference necessary to maintain equilibrium of the solvent in a solution with a more dilute solution (or the pure solvent) at a lower temperature has been called the 'osmotic temperature'."

**The definition from the same source as for the above: "A solution in which there is a gradient in temperature shows a gradient in composition also."

> mole of component A of a binary solution between regions of differential temperature difference in an infinitely large tube. The withdrawal of A from the solution at T produces an infinitesimal change in concentration. In the general case this change in concentration may be assumed to give rise to a corresponding change in the intensity of intermolecular forces. The adjustments occasioned by the change in forces, extending throughout the infinite quantity of solution, may result in a finite heat effect. Assuming, therefore, a quantity of heat $\overline{Q}_A$ to be absorbed from the reservoir at T, and given out at T+dT, where the reverse change must occur, the change in entropy in the reservoirs from this cause is $\overline{Q}_A dT/T^2$. In addition there is the exchange of entropy between the reservoirs and the system of $d\overline{H}_A/T$. The total change in entropy of the reservoirs is then
>
> $$\delta S_R = -d\overline{H}_A/T - \overline{Q}_A dt/T^2$$
>
> $$= -(1/T)\ [(\partial\overline{H}_A/\partial T)_{P,N} dT + (\partial\overline{H}\ /\partial N_A)_{P,T} dN_A] - \overline{Q}_A dT/T^2$$
>
> The entropy change of the system remains
>
> $$\delta S_S = d\overline{S}_A = (\partial\overline{S}_A/\partial T)_{P,N} dT + (\partial\overline{S}_A/\partial N_A)_{P,T} dN_A."$$

This concept of the difference between δS_R and δS_S is of fundamental importance for the electrodynamic model, and the recombination of the two into $\delta S_R + \delta S_S = 0$ for virtual transfers under equilibrium condition, by which this type of analysis is usually concluded, must be avoided since it does not require any understanding of the spatial distribution of the process and therefore conceals the most important aspects.

In Eastman's third paper[165c], a further development on the theory of Soret effect is discussed, and the definitions of his "heat and entropy of transfer" are fully presented --

> "When a portion of one of the constituents of a solution is transferred by diffusion, or in the case of ions by an applied electric field, from one region to another within the solution, there is in general an accompanying absorption of heat from the surroundings of one region and evolution in those of the other. The quantity of heat absorbed from the surroundings of the region (of infinite extent) from which one mole of constituent A is transferred will be denoted by Q_A^*. The entropy lost by the surroundings [*numerically different from the entropy gained by the system*] of the region from which the transfer is made is then $Q_A^*/T = S_A^*$. These quantities will be referred to as the heat and entropy of transfer respectively."

He then suggests that the total Soret effect should be considered in two parts --

> "These parts would be associated, respectively, with the free energy change due to the concentration gradient and that due to the electrical gradient. The latter part of the effect may, however, be seen to be negligible compared to the first. Owing to the very strong forces between ions of opposite charges, the gradient in ionic composition must be extremely small. The number of equivalents of positive ions transferred in establishing equilibrium, or in returning to the normal condition after removal of the temperature gradient, is therefore almost exactly the same as that of negative ion."

From the above considerations Eastman deduces a very clear description of the energy distribution within an electrolyte --

> "The free energy difference per mole of either ion transferred in such diffusion, which is the product of the difference in number of equivalents of oppositely charged ions, and the potential difference between which they are moved, must be negligibly small even though the potential difference itself is not."

which, may be considered as the best analysis of the old question as to where, within an electrolytic cell, is the seat of the emf located.

The analysis of the heat changes associated with the emf generation is the most outstanding part of Eastman's work, as far as this investigation is concerned. The fundamental concepts are indicated in his first paper[165a] and the full treatment is developed in his fourth[165d]. The two works will be considered together in the review following.

His definition of a thermocouple is most interestingly based on the concept of metals being solutions of ions and electrons, thus a thermocouple --

> ".... may be regarded as a two-phase system of the three components M_1^+, M_2^+ and E^-. The electrons E^-, are mobile, while the ions of the metals do not move appreciably under an electric force."

Then, in analogy with the treatment indicated earlier, Eastman proceeds to calculate the entropy changes for the system (two metals and electrons) and for the reservoir (the surroundings) when a mole of electrons is transferred through the thermoelectric circuit. He defines --

> ".... the partial molal heat content of electrons in the two metals $\overline{H}_E'$ and $\overline{H}_E''$, respectively, the heat absorbed at the junction b [*at T+dT*] and given out at c [*at T*] is $\overline{H}_E' - \overline{H}_E''$, or $\Delta\overline{H}_E$. The heat exchange between system and reservoir is dH_E'. We can write therefore,
>
> $$\delta S_R = \Delta\overline{H}_E dT/T^2 - d\overline{H}_E'/T$$
>
> and
>
> $$\delta S_S = d\overline{S}_E'.$$
>
> Noting that $d\overline{H}_E'$ and $d\overline{S}_E'$ depend only upon the difference in mole fraction of electrons, N_E', in

> the regions a and d [*the open terminals of same metal*] [...] the work which could be obtained on transfer of a mole of electrons directly between d and a. It is the e.m.f., dE, of the couple. The heat effect at b corresponds to equilibrium conditions and is equal to $T\Delta\overline{S}_E$. We obtain therefore --
>
> $$dE/dT = \Delta\overline{H}_E/T = \Delta\overline{S}_E$$

Finally, Eastman proceeds to distinguish between electrolytic thermocouples (defined in section II,0,4 of this thesis) and thermocells, which have a cell arrangement that is most relevant to this investigation. Thermocells are represented schematically as follows --

$$\text{Electrode} \underset{T_2}{|} \text{Solution} \underset{T_1}{|} \text{Electrode}$$

and Eastman's[165a] Fig. 2 - Diagram of a thermocell, is reproduced in Fig. II,1 .

At this point it is appropriate to reproduce Eastman's entropy and heat analysis for thermocells, since this is the only work which clearly indicates the existence of the anodic cooling effect --

> "At equilibrium, electrons will be at different concentrations (but the same temperature) in the metal at a and at d in Fig. 2. When a mole of electrons is used up from the mercury in a b [*the cathode*] and produced at c [*the anode*] by reversible electrode processes and then transferred to d, certain entropy changes occur. If these are formulated in the usual way, it is found that only two factors are of final significance, that is, are not eliminated in combining δS_R and δS_S in equation 1 [$\delta S_R + \delta S_S = 0$]. These two factors are the difference, dF_E, between the partial molal free energies of electrons in the

> metal at d and at a, and the heat absorbed in the electrode reaction at c. The equation for the latter reaction in the example given may be written --
>
> $Cl^-(0.01\ M\ HCl) + Hg = HgCl + E^-(Hg)$ [*anodic reaction*]
>
> (I)
>
> Since the reaction occurs under equilibrium conditions, the heat effect in it is equal to $T\Delta S_S$, where ΔS_S is the increase in entropy of the system accompanying the reaction I. The relation involving these quantities which is finally obtained is [*from Eastman's fourth paper* [*165*d] *eq. 4*] --
>
> $$FdE/dT = \Delta S_S + \Delta S^*$$
>
> In this equation ΔS_S is the entropy gained by the system at higher temperature in the electrode reaction caused by one faraday passing from left to right through the cell. ΔS^*, again is the net entropy of transfer of ions, is now given by --
>
> $$\Delta S^* = t_c S^*_c - t_a S^*_a".$$

In the above reproduction, only the subscript for the system entropy change symbol has been changed in order to unify the terminology used by Eastman in his first and fourth papers; t_c and t_a are cathodic and anodic transport numbers respectively.

In closing, Eastman states --

> "The heat effect in reaction (I) is no doubt directly determinable experimentally (though under irreversible conditions, so that only approximate identity with $T\Delta S_S$ might be claimed) by methods devised for the study of Peltier heats."

This is precisely the aim of the experimental part of this thesis, but the use of methods devised for the study of Peltier heats is regarded as not appropriate, as it will be discussed in section II,07 by reviewing the work of Thouvenin[125].

In summary we can see that the entire work of Eastman is based on the very interesting concept of entropy of individual ions, in fact this is the only type of thermodynamic treatment appearing in the literature, developed for a half-cell reaction only.

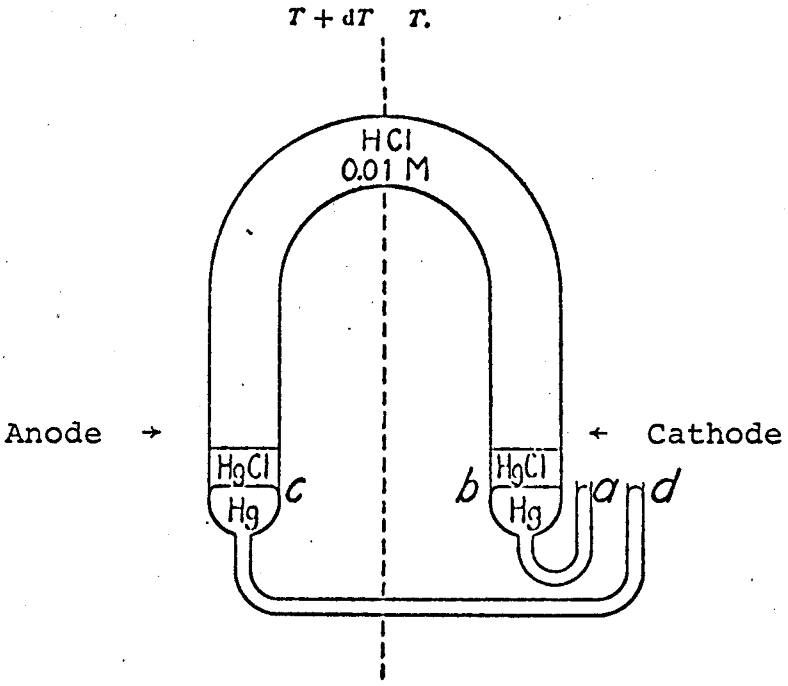

Fig. 2.—Diagram of a thermocell.

Fig. II,1 - Reproduced from Eastman[165a] with the addition of Anode and Cathode labels.

G. ELECTRODE REACTION MECHANISMS

1. Introduction

In an attempt at distinguishing amongst the various approaches in the investigations of electrode processes, the various authors are divided into two groups -- one group which regards the electron transfer from the metal electrode into solution as the central mechanism, and the other group where the ion transfer from solution to the electrode metal surface is the assumed reaction mechanism for the case of cathodic deposition of a metal.

2. Electron Transfer Mechanism

The first attempt at a scientific approach to the theory of electron transfer at electrode-electrolyte solution interface was made by Gurney in 1931[21,22,23,24], who investigated the reaction:

$$H_3O^+ + e^- \rightarrow \text{products}$$

He considered the energy of the system just before and just after neutralization of the H_3O^+ by an electron, which comes by a tunnelling process from the electrode. The effect of applied potential was described as a lowering of the effective work function of the metal. Gurney deserves the credit for having introduced into the system the attractive energy of interaction between the proton and the water molecule, and the repulsive energy of interaction between the atomic hydrogen, just neutralized, and the molecule of previous hydration. Furthermore, he predicted the decrease of the current density values upon increasing the value of the work function.

However, Gurney's approach is still oversimplified since the protons in solution possess a distribution of rotation, libration, vibration energy levels, and the activation energy levels obtained by Gurney are very high when compared with the experimentally determined value; (this is not to say that the experimental values are necessarily the correct ones).

The first to give a graphic representation of the activation energy barrier for electrode processes was Eckhart [25]. The effect of potential on the barrier shape was accounted for by superimposing a linear field on a symmetrical barrier. The potential energy expression was obtained as a function of the predetermined values of barrier width and activation energy.

Ogg, Horiuti, M. Polanyi and the Evans[26 to 32] first used the potential energy versus distance curve to describe the discharge reaction, as it is still used today. The works of J.C. Polanyi et al[33,34] demonstrate the high degree of development that this concept is having in molecular physics today, where it has been extended to energy surfaces.

Marcus[35,36,37] is regarded as the one who best translated these treatments of homogeneous reactions* into terms suited to reaction at electrodes. His theory permits the determination of the parameters on which the energy of the activated complexes depend. However, he treats heterogeneous reactions as homogeneous, in the classical mode of motion along the reaction coordinate. He treats solvent polarization by statistical mechanical method of the equivalent equilibrium distribution, and includes ligand reorganization energy in a quadratic approximation. It is most interesting, however, that he suggests[37] that, for metals, the energy levels making the major contribution to the rate of reaction lie at κT above the Fermi energy level of the metal. With regard to the last point, a brief digression is worthwhile to consider the implications contained therein -- at 300°K those levels making the contribution are about 1/40 of eV above the Fermi level; if the electrode is set at a potential energy of 1. eV lower than the solution, could it be said that the energy density difference between the electrode and the solution, expressed in terms of absolute temperature, is of the order of 10^4K?

The most recent and possibly the best application, so far, of Marcus' theory to the study of the variation of the charge transfer coefficient (α) value with various

---

* Marcus' works on chemical dynamics are cited in the previous references.

electrochemical parameters is offered by Bonnaterre and Cauquis[38]. They proposed an equation for the voltamperometric curve where α is expressed in terms of the externally applied potential difference, of the ionic diffusion coefficient, of the thickness of the double layer, and of the reorganization parameter. The agreement with experimental results is not too close, thus these authors gave an expression for the relationship between the apparent value α, experimentally determined, and the value α, from Marcus' theory. Could this difference be due to the fact that they did not account for energy-temperature variations along the reaction coordinates?

Hush is apparently the only one who developed first a reaction model for processes at electrodes (1958)[39], then subsequently used this model to derive a model for homogeneous chemical reaction (1961)[40]. This last work was criticized among chemical physicists in the relatively few instances in which his work is mentioned. I regard the initial part of his treatment as very good, especially in that he presents very clear definitions of the starting assumptions made -- adiabatic process, transition state described by a single eingenfunction, mass vibration decomposition, mean velocity of crossing the barrier, Born-Oppenheimer approximation, role of the dielectric. Hush is one of the very few who openly questioned the significance of estimating the energy of activation of the electron-transfer step, by the construction of energy profiles from constant-charge, energy-distance curves. He goes on to suggest the replacement of the above method by the calculation of the energy as a function of the electron density on the solution side of the interphase. In fact, the key concept of his theory is the variation of distribution of electron charge density during the course of the reaction. Following this line of thought, he stated that the ion in the transition state is only partially charged, and that there is no correlation between the ionization potential and the rate constant.

Clearly this last statement cannot be accepted since the deionization potential energy is the measure of the natural tendency for the neutralization reaction to occur, and the electron-transfer act is, by far, the shortest lived reaction, thus the species are always either neutral or charged. Nevertheless, his graphical representation of the activated complex reaction path together with the synchronus variation of the electron density, is worth expanding on, mostly in view of the clear physical representation of the resonance effect, which agrees with Hagstrum[41] treatment of surface energies.

Hush's approach is very useful in the formulation of the electrodynamic model, even if he dismisses the problem of explaining how deactivation occurs by saying --

> "In passing over the energy barrier, vibrational energy is converted into energy in other degrees of freedom of the system; the transition ion M^q being in its ground vibrational state."

In this statement Hush recognized the existence of an amount of energy produced by conversion of vibrational energy after the transition stage, but he neglects it by assuming the transition ion in its ground vibrational state.

The development of the views of the electron-transfer group of the Russian school is presented by Levich et al.[42,43]. They have followed the classical sequence of first proposing models and expressions for homogeneous reaction, then, adapting it to the requirements of electrode processes. It is probably the most elegant exact quantum mechanical treatment of electron transfer reactions; but, in line with what appears to be a characteristic of the Russian school, several omissions and simplifications, that were made to achieve the exact mathematical solutions, reduce the usefulness of the method.

More recently, however, this group has curtailed their elegant treatment, and a more comprehensive, correct physical interpretation of the parameters has resulted[44]. It has replaced the harmonic oscillator approximation with the Morse curve when the reagents are in the form of solvated ions complexes. It is among the few who attacked the theory of absolute reaction rates because of the assumption that the motion of the system over the energy surface during the reaction process is classical (as defined below) and only the electrons are treated as a quantum system. They stressed that the whole electrode system should be divided into two subsystems -- a quantum subsystem (electrons and intramolecular degrees of freedom having frequencies $\omega > \kappa T/\hbar$) and a classical subsystem (solvent and molecular degrees of freedom with excitation energy $\Delta E < \kappa T$). They define a thermal effect, composed of both the quantum and the classical part, corresponding to the difference between the minimum energies of the final and initial state. The total probability for the elementary act depends on that difference.

For the case of hydrogen evolution reaction, they stress that thermal energy cannot activate the $H^+ - OH_2$ bond to a higher vibrational level (by stretching as assumed by Gurney) because for this bond $\hbar\omega > \kappa T$. Instead, Levich[44b] proposes another mode of activation -- the solvent fluctuation -- which can be described as follows: - as the solvent dipoles around the central ion fluctuate the energy of the ion also changes, and for a particular orientation of the dipoles, the ions get enough energy so that a radiationless charge transfer become possible. - His calculations show that for a reaction with an activation energy of the order of 0.5 eV, the water molecules within a radius of 20 Å from the ion, must fluctuate.

This most important concept is in agreement with the dynamic characteristics of the electrode/electrolyte interphase of the electrodynamic model.

After this promising start, they use the assumption that the quantum subsystem is in an unexcited level both in the initial and the final states; they concede, however, that the potential energy surface should be regarded as a function of the coordinates of only the classical subsystem and the surfaces of initial and final states have different numbers of measurements.

Somewhat in agreement with Marcus, they find that their expression for the calculation of the current gives a sharp maximum at a certain energy level ε^* characteristic of the particular electrode system, and the contribution to the current is made by only a narrow range of electronic levels in the metal. This fact, coupled with the use of the Bronsted microscopic equation, gives them the possibility of dividing the various electrode processes depending on how ε^* compares with the Fermi energy level of the metal -- low overpotential or barrierless region, normal region, high overpotential or activationless region. This approach appears to be useful for more precise description of the physical meaning of the charge transfer coefficient.

Recently, Dogonadze and Kuznetsov[45] expanded on the above treatment by proposing a semiphenomenological theory of electrochemical reactions, with the aim of dispensing as much as possible of the model hypotheses of the quantum mechanical theory. The key concept is that in the course of cathodic reactions free electrons from the metal electrode pass to discrete isolated final-state levels to independently discharge the ions and thus generating the current. This concept of current generation at the electronation point, is one of the most important bases of the electrodynamic model; and as it will be discussed later, the commonly used statement describing the electrode process in terms of a charged species crossing the electrolyte-electrode interface is regarded as wrong. In agreement with Hush's treatment, it is assumed that, despite the flow of current the filling of the energy levels is quasiequilibrium in nature. In particular, they treated the intermediate regions within the above division, that is, the quasinonbarrier and quasinonactivation.

This group of authors has also studied the simultaneous transfer of two electrons to a divalent ion from the energetic point of view[46]; thus they have thrown some light on the controversy on whether the present theory of two one-electron transfer steps (Conway and Bockris)[59], or a single two-electrons transfer-at-once is the true mechanism for divalent ions electrode processes.

The expert in these multiple electron transfer reactions seems to be the Losev group[47,48], which very recently summarized this topic for the case of amalgam electrodes[49], and with regard to behavior of the low-valency intermediate.

Devanathan[50] has studied fast-multi-electron-transfer reactions, and concluded that all the electrons cannot be transferred in one stage but only by a succession of single electron-transfer steps; and it is improbably that all these steps have the same rate constant. Further, the electric field at the interface will influence the course of the reaction at every stage since each involves charged particles; the transfer coefficient will therefore be a complex quantity for such reactions. The last statement, transformed in terms of field strength, is one of the bases of the electrodynamic model.

In this context, a very recent treatment by Conant and Houseman[51a,b], for the first time, proposes an expression to determine n (the number of electron transferred in the reaction) as a function of the metal dissolution in the electrolyte and of the electronic conduction of the electrolyte. Its value turned out to be far from the exact integers commonly used in the determination of activities of metals by emf measurements. The existence of this problem, however, was pointed out earlier by Hager et al.[52,53,54].

What is most interesting is that the value of n is a decreasing function of the current density, as reported by

Conant and Houseman for the Cd-I system -- 1.9 for low current density to 1.5 for limiting high current density. The tentative explanation offered by these authors in a private communication was that the lower valency ion fraction is kinetically more able than the higher ones. This is certainly a most interesting field worthy of further investigation.

This section will be concluded by reporting some of the comments Reynolds and Lumry (1966)[55] have made on electron transfer theories, which are still valid today --

> At present there is very little understanding at experimental or theoretical levels of the temperature dependence of the electron-transfer reactions. The comparison of the free energy of activation [*calculated vs. experimental*] are only partially useful -- enthalpy and entropy values should be compared. However, reasonable agreement between calculated and experimental values for ΔG^*, but complete disagreement on ΔH^* and ΔS^* have been reported. The calculation of the interaction energy between reactants and products is an ordinary straight-forward quantum-mechanical calculation and should yield more accurate values about the turn of the century.

Further, these authors made a very interesting observation --

> "since over-all free energy changes in most chemical reactions are small relative to the promotion energies to excited states, in reactions with a large negative over-all free energy change the products may be formed in excited electronic states; it is to be expected that these processes will be found to emit radiation in the de-excitation of the products."

This last statement brings us into the fascinating field of photoelectric effects at metal/electrolyte interphases, also called galvanoluminescence, which, unfortunately, lies beyond the knowledge of the author of this thesis.

3. Ion Transfer Mechanism

Butler[56] applied the graphical representation of Horiuti and Polanyi to Gurney's theory. The potential energy curve versus distance for the $H^+ - OH_2$ system, to obtain a distance at the crossing point; thus, he was the first one to introduce the proton transfer concept. This crossing point only meant that the electron transfer could take place at distances from the electrode smaller than that of the crossing point. However, the proton transfer distance was extremely small (0.3A), primarily because he used a high fundamental frequency value (3,660 cm^{-1}); this type of calculation will be discussed in the development of the electrodynamic model. The important improvement to the theory was to account for the energy of adsorption of atomic hydrogen onto the metal, which lowers the calculated value of the required activation energy. Unfortunately, Butler did not emphasize the concept that the two curves belong to two different time periods, ie., before, and after the act of electron transfer, and that the crossing poing has no meaning other than that mentioned. This lead to erroneous interpretation by most researchers who have followed this approach.

Parsons and Bockris[57] also applied the Horiuti and Polanyi potential energy profile construction to the calculation of the energy of activation of discharge of hydrogen ions at metal electrodes, and they were the first ones to attempt the calculation of the symmetry factor β. They calculated the activation energy of the hydrogen discharge reaction on mercury and nickel surfaces allowing for all possible variations of the parameters used.

Later Despic and Bockris[58] used this treatment to explain the dependence of the symmetry factor on potential for the electrolytic dissolution and deposition of silver. The potential energy curves used to represent the course of the reaction were drawn on the basis of experimental data to locate the distance between the potential energy minima, and the double layer width, and on the basis of thermodynamic data to determine the energy difference between initial and final states, in equilibrium conditions.

Conway and Bockris[59,60] have taken into account a variety of possible ways in which the ion transfer from solution to metals may take place, all involving mechanistic considerations of sites, steps and kinks on the electrode surface where entities by names of "adion" and "adatom" are wandering. They calculated all the relative energies for each of the above possibilities for the reduction of Cu^{++}, Ni^{++} and Ag^{+} and concluded that these mechanisms are improbable.

The mechanism of electrodeposition of metals in general has been only treated in terms of Ion Transfer approach. A summary is offered by various works of the Bockris group [61,62,63] and others[64,65].

The author's direct knowledge of Gerischer's work is very limited[66,67] due to a lack of knowledge of German language. Nevertheless, Gerischer's finding[66] that the exchange current value for mercury electrodes is the same for liquid and for solid mercury at the melting point is considered to be significant.

In this context, Bockris and Enyo[68] studied gallium liquid and solid electrodes finding that at overvoltages < 0.1 V the current is higher on liquid than on solid electrodes, for the same overvoltage; while in the 0.1 V region the current is almost the same for both. Above 0.1 V, however, besides the interpretation given by these authors in term of surface diffusion, from the plot given one could see a parallel behavior (same slope) with the solid line some 20 mV higher than the liquid one, at the same current. As it will be seen, this fact is in agreement with the physicochemical characteristics of the selvedge of the electrodynamic model.

Frumkin's group has provided outstanding contributions in the early days of electrochemistry (development of the exchange current density, etc.), however, in my opinion, it tends to adhere to oversimplified exact analytical treatment of electrode systems. An example of the above tendency is shown in their comments[69] on Devanathan's work on the structure of the metal/solution interface. I am sure that this opinion of mine must be due to lack of knowledge of

Frumkin's work. In fact I could not find a comprehensive treatment in the literature or a textbook by this author presenting his views on all aspects of electrochemistry -- similar to that which is available on Bockris, Vetter, etc. -- mostly papers related to the concept of adsorption. Demaskin in his monograph on methods for studying electrochemical reactions[70], states that the structure to the electrical double layer is not to be taken into account since it appreciably complicates the mathematical treatment. However, he includes corrections to electrochemical reaction parameters which are obtained without considering the structure of the double layer. Dogonadze and Chizmadzhev[71] attacked Marcus' theory for not being able to calculate the exchange current, but the expression they proposed is based on the following assumptions:

- charge transfer coefficient $\alpha \equiv 0.5$,
- interreactant distance of arbitrary constant value,
- preexponential factor of their own estimation,
- use of a constant equal to the difference between the reciprocal of optical and static dielectric constant,
- constant energy of transpolarization $\simeq 10.$ eV.

They conclude that the comparison of their treatment with experimental results is (in 1962 but also to date, as is apparent from the synopsis of this thesis) a matter of some difficulty because of the lack of reliable experimental data on the coefficient α. They offer, however, some interesting points regarding the fact that the double layer is weakened by the ions undergoing discharge, and that their harmonic potential energy curves do not include the kinetic energy of the solvent species and further that the electrons are at "some" energy level of the metal, different from the Fermi level.

The above division of authors into two categories -- electron-transfer and ion-transfer -- is not artificial or fictitious but represents a real state of antagonistic positions. In one of the most recent Frumkin's papers[72], we can see to what extent this quarrel is still going on nowadays; in this particular paper this author disputes J. Butler et al. electronic views which questioned the validity of his adsorption energy and ψ effect mechanism.

H. MOLECULAR DYNAMICS AND EYRING'S RATE THEORY

It seems appropriate to follow the section on ion-transfer mechanisms with a few words about the latest development on the most important theory in this field -- Eyring's Rate Theory, also known under the names of Activated-Complex Theory, Absolute-Rate Theory, and Transition-State Theory.

Laidler and Tweedale[73] recently reviewed and improved it by proposing a Vibrational Adiabatic model, which in my opinion comes very close to Hush's approach. This can be taken as an indication of the trend towards an ultimate combined treatment of electron and ion transfer. These authors recall the special type of equilibrium in which the activated complexes are assumed to be with both reactants and products, and restate the "enormous simplification" introduced by considering only the concentration of complexes and the <u>speed</u> with which they cross the barrier -- which works if reliable experimental values for the activation energy are available and reliable guesses on the structure of activated complexes can be made. Further, there are two classes of activated complexes, those that were reactants and those that were products. The flow of complexes in one direction is independent from the flow of the other class of complexes in the opposite direction. The peak of the classical energy-distance diagram (Fig.I,1) is considered as the point of no return for the transient species, which is not a species undergoing a number of vibrations thereby coming to equilibrium, rather, the maximum in the curve is passed straight in one direction during a time of the order of 10^{-14} sec.

Eyring's theory can be used to obtain valid results for slow reactions near the equilibrium; for $\frac{E}{RT} < 5$, however, the dynamic behavior of the system must be considered, and Laidler and Tweedale used Karplus data on energetics of collision for $H\text{-}H_2$ system to develop their vibrational adiabatic model.

The criticisms made by Levich's group on Eyring's theory regarding the classical treatment of quantum systems are still valid for this new development. The highlight of this work, however, is the accounting of the various energies stored, transferred, and used for crossing the barrier. This result in an amount of energy which is not used for crossing the barrier, and thus remains stored in stretching modes of the activated complex. Laidler and Tweedale called it --

> "Some adiabaticity of vibrational energy which can not be freely converted into energy required to cross the barrier; some of it must remain as vibrational energy."

It is most interesting that this "remaining energy" is comparable (of the same order of magnitude) with the energy required for crossing the barrier.

In view of the importance to this thesis of this type of calculations in which molecular dynamics data are used for the description of activation processes far from equilibrium, a summary of Laidler and Tweedale calculation is given in Fig.II,2 in which the H-H_2 system is quasi-classically treated as follows:

- vibrational and rotational states in H_2 molecules are quantized, but the course of collision is treated classically;
- on H-H_2 energy surface the collisions are of very short duration -- 10^{-14} sec;
- for the potential energy surface the barrier height is 9.1 Kcal with respect to the classical ground state;
- trajectory calculations give a minimum of 9.4 Kcal of relative translational energy required for the system to cross the barrier;
- this 0.3 of extra energy is stored in symmetrical vibrational mode of the H..H..H complex and does not contribute to crossing the barrier;
- the zero-point vibrational energy of initial state is 6.2 Kcal;
- thus, the minimum energy required to cross the barrier from zero-point level (9.1 - 6.2) = 2.9 Kcal;
- calculations for classical trajectory for linear collision in which H_2 is at zero-point vibrational level, give a threshold energy of 5.3 Kcal;
- thus, 2.4 Kcal (5.3 - 2.9) of energy is forced into the symmetric stretching vibration of the activated complex;
- thus, of the 6.2 Kcal of vibrational energy available, only about 3.8 Kcal can contribute to the reaction.

Laidler and Tweedale improved somewhat Marcus' and Hush's type of graphical representation of energy profiles by imposing a floor on the potential energy surface corresponding

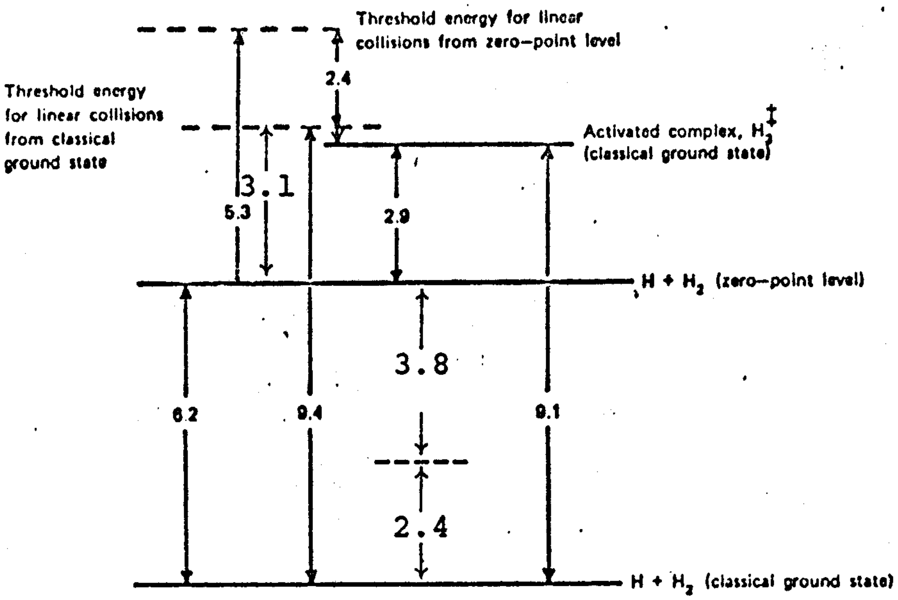

Fig. 2. Energy diagram for the H + H_2 system, showing energies for linear collisions (classical calculations of Karplus et al.).

Fig. II,2 - Reproduction from Laidler and Tweedale[73]; the larger type numbers have been added as discussed in the text.

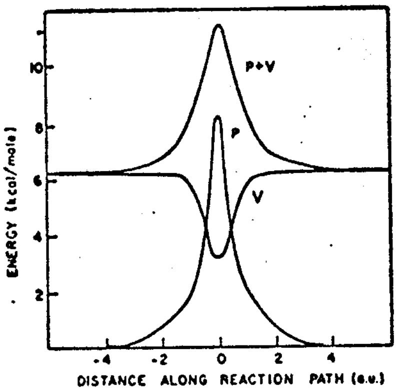

Fig. 4. Energy profiles for the H + H_2 system; curve *P* is the classical potential-energy profile; *V* shows the variation in the zero-point vibrational energy; *P* + *V* is the resultant of the two.

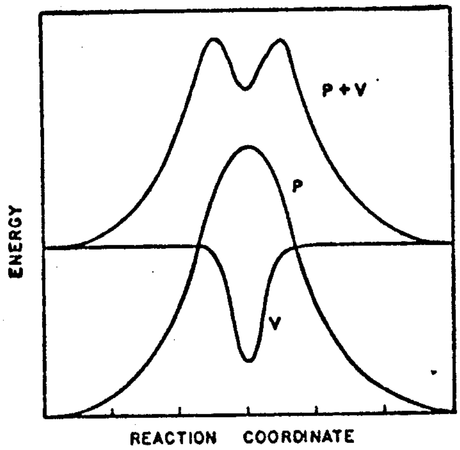

Fig. 5. Schematic energy profiles showing how *P* + *V* can involve a double maximum.

Fig. II,3 - Fig. II,4 -

Both figures are reproduced from Laidler and Tweedale[73] without editing additions.

to the zero-point energy at each point along the path. Incidentally, these authors are among the very few who give numerical values for energies and distances. What is very interesting is that they are able to show separately, the contribution of the classical potential energy and that of the zero-point vibrational energy, as shown in Fig.II,3 where, for the H-H_2 system --

P - classical potential energy curve from Karplus surfaces,

V - variation of the zero-point vibrational energy,

P+V - resultant energy profile from the summation.

As mentioned previously, the key concept of this representation is that at all points along the reaction path, the vibrational energy normal to the path must always be the zero-point energy -- the rest of the energy is available for crossing the barrier. Thus, as we see in Fig.II,3 the V curve dips in the neighborhood of the activated state, and simultaneously the P curve rises. The energy available for crossing the barrier is the difference between the minimum of V and the maximum of P.

Another most important observation is that, not only does the value of the maximum of the curve P+V depend on the individual shapes of the P and V curves, but also its shape. In fact, with a V curve having a sharp minimum and the corresponding P curve having a wide gradual maximum, we obtain two maxima for the resulting P+V curve. Thus, the true energy barrier would not lie at the col but it would lie to the sides of it, and the activation energy would necessarily be higher than the height of P+V maxima (see Fig.II,4).

Laidler and Tweedale conclude their work by stressing the great value that more detailed treatment will have in providing information not given by the activated-complex theory, namely information about energy distribution in product molecules, i.e. how the 2.4 kcal stored in the activated complex is disposed of during the deactivation of the complex. As mentioned in the Introduction, this is exactly the focal point of this thesis.

I. THE EXCHANGE CURRENT DENSITY

This pre-eminently dynamic phenomenon is responsible for the true thermodynamic equilibrium existing at the electrode/electrolyte interphase.

As reported by Vetter[153], this concept was first mentioned by Butler[56] (1936), then Bowden and Agar (1938) used it, and Dolin, Ershler and Frumkin (1940) developed the treatment and gave it its appropriate name.

Later, Gerischer and Vetter (1950-55) widened its application beyond the hydrogen electrode; but no important theoretical improvement to further develop the concept, appears to have been accomplished since. What follows is a summary of a recent description by Vetter[153] of the exchange current density phenomenon --

> "On a molecular scale, a constant exchange of charge carriers (ions or electrons) take place through the phase boundary. This exchange corresponds to identical anodic and cathodic current densities that compensate each other at the equilibrium potential, so that no external current flows, and no macroscopic reaction takes place. The magnitude of this mutually compensating current densities at equilibrium potential, is called exchange current density i_o. By definition, i_o is positive and is a measure of the rate of equilibrium potential formation and sensitivity to interference [*external perturbations*].

Bockris and Reddy[2], under a section heading called Two-Way Electron Traffic Across the Interface, gave their views which have been summarized as follows --

> "Principle of microscopic reversibility -- what can happen in one direction can also happen in the opposite direction. If positive ions can move from solution to the electrode [*any process which can occur in one direction can also occur in the opposite direction*], they can also jump back in the opposite direction. If the directed field hinders the ion transfer from solution to electrode, it helps along the jump in the opposite direction. The explanation of why the electronation reaction does not come to a halt, is because the de-electronation reaction is splitting a neutral atom into an ion and an electron, and thus putting electrons into the metal and opposing the increase of positive charge on the metal. There must be some value of the field, or potential difference, at which the electrode's rate of loss of electrons (the electronation reaction) and its gain of electrons (the de-electronation reaction) must become equal. Thus, there is an equilibrium potential difference across the interface characteristic of the reaction. Beneath the apparent lack of motion, charges pass constantly to and fro across the interface. The electronation and de-electronation continue to occur, but at the same [*equal*] rate. The significance of these equilibrium currents is that they are a quantitative measure of the rate of reaction which occurs in opposite directions at equal rates, at an interface at equilibrium; they numerically express the rate of the two-way electron traffic between the electrode and particles [*species*] in the electrolyte. They characterize the rate of the electron exchange between the metal and the solution under equilibrium conditions. The equilibrium exchange current density is like [*can be likened to*] a one-dimensional random walk of electrons across the interface with equal number of electrons walking in both directions.
>
> Regarding the experimental determination of the numerical values of the equilibrium exchange current densities, all authors agree on the impossibility of measuring them with an electron drift measuring instrument, since there is no net electron drift because of the absence of a net chemical transformation given by the difference between de-electronation and electronation reactions.

The various methods used for its determination are mostly based on the use of the Tafel relation assuming a certain value for the charge transfer coefficient.

The only established experimental finding is that the value of the exchange current increases with temperature; whereas its dependence on the ionic concentration does not seem to be fully determined. Very recent works by Schuldiner and Rosen[154], and by Dirkse and Hampson[155] deal with this subject.

In conclusion, we can make three important observations: all authors, in their treatment of exchange current, always use the term "interface", even though (as in the case of Bockris[2]) they have used interphase in other sections of their electrochemical treatments;
the identity of the charge carrier is left undetermined;
in all honesty it cannot be said that the physical picture -- the energetics of this phenomenon -- as it is currently described, is satisfactory.

The seriousness of this lack of knowledge about the exchange current cannot be overstressed, primarily because its close interconnection with the charge transfer coefficient, can be regarded as the central concept of electrochemical kinetics. In fact, in one of the latest works on electrocatalysis, Bockris, McHardy and Sen[156] still had to assume a semi-empirical constant value for the charge transfer coefficient in order to develop their analysis resulting in a linear dependence of the efficiency of electrochemical systems on the logarithm of the exchange current density.

J. COMBINED PROTON AND ELECTRON TRANSFER

The situation illustrated in the previous sections began to improve about 1966 when Bockris and Matthews[74] first proposed a combined treatment of proton and electron transfer theory. In view of the importance of the hydrogen evolution reaction in metal electrodeposition systems, and since this type of approach is pursued in the formulation of the electrodynamic model for metal ion electrode processes, Matthews' thesis[75] will be commented on to a larger extent than was done for the preceding authors.

The expression for the determination of the Activation Energy values used by Matthews is the Temkin "real" activation energy: ([75] p. 107)

$$E^* = -R\{ d \ln i / d\,(1/T)\}_{\eta,a}$$

where:

$$\{d \ln i / d\,(1/T)\}_{\eta,a} =$$

$$= -\Delta H_o^*/R - \alpha F\Delta\,\phi_{rev.}/r - \alpha F\eta\,/R - (\alpha F/RT)\;d\Delta\phi_{rev.}/d(1/T)$$

and:

R, F - gas and Faraday constants respectively

T - absolute temperature

η - overpotential at current density i

a - Tafel constant, independent of i

α - transfer coefficient

$\Delta\phi$ - absolute electrode potential

The experimental determination of ΔH_o^*, the standard enthalpy of activation, is difficult because of the difficulties in maintaining the potential $\Delta\phi$ constant with changing temperature. Thus a correction is made using the temperature coefficient of the Absolute Electrode Potential value, d $\Delta\phi$ rev/ dT. This correction, however, refers to equilibrium conditions only, hence is not strictly true for the case under consideration. The charge transfer coefficient α, is assumed constant over a wide range of potentials. As pointed out reviewing Marcus' work this is not the case. The intercept of the Tafel equation, a, is taken to be constant for all current densities. Again this is an oversimplification.

Matthews goes on to calculate the number of electrons with energy greater than the activation energy using the theory of thermionic emission. In section II,N of the development of the electrodynamic model it will be shown that this is not a valid procedure. He also uses the Boltzmann distribution, instead of Fermi-Dirac statistics (he will justify this assumption later) for the H_3O^+ vibrational-rotational energy levels to calculate the number of intermediate states (M--H--OH_2) with the required minimum energy. He then states --

> "When the H^+ is neutralized at a given energy level it forms a H atom which interacts with H_2O and the metal surface, with an interaction energy dependent on its distance from these nuclei and hence on the original vibration-rotation energy level of the H_3O^+ ion".

In this statement, Matthews just misses the concept of excess energy. That is, he did not account for the energy released in deactivation process. The reason for this, as is pointed out in the next paragraph, is the incorrect use of the potential energy curves concept ([75] p. 402):

> "....if we were to give equal quantities of energy to the electron in the metal and to the H^+--OH_2 bond . . . favoritism of H^+--OH_2 excitation as compared to electron excitation . . . [*will result*]...."

Fig.II,5 illustrates Matthews' graphical interpretation of the mechanism of the hydrogen evolution reaction and he presents the following arguments --

> "....Imagine that an electron from the Fermi level of the metal tunnels to the excited H^+--OH_2 at the energy corresponding to point X. The intermediate state $(M$--H--$OH_2)_{DL}$ is then formed, as a consequence of the neutralization act. The H experiences repulsion by the H_2O and attraction by M so that the H atom moves toward the electrode and the energy of the system changes according to curve (b)."

On the confusion between potential energy and energy, which is the difference in potential energy, we will discuss in section IV,4 of the development of the electrodynamic model.

Referring to Fig.II,5 Matthews continues --

> "....for this process point X thus refers to the activated state which is identical with the above mentioned intermediate state. Next, consider an excited electron on the metal, i.e., an electron in an energy level above the Fermi level. The state of the system is then raised vertically a distance $\Delta\varepsilon$ above the former curve. As the H^+--HO_2 is stretched the energy of the state changes along the curve (c), identical in shape to curve (a) till such a point X' that the excited electron in the metal may tunnel to the excited H_3O^+ ion. The energy of the system then changes, as before, according to curve (b). In the first case the

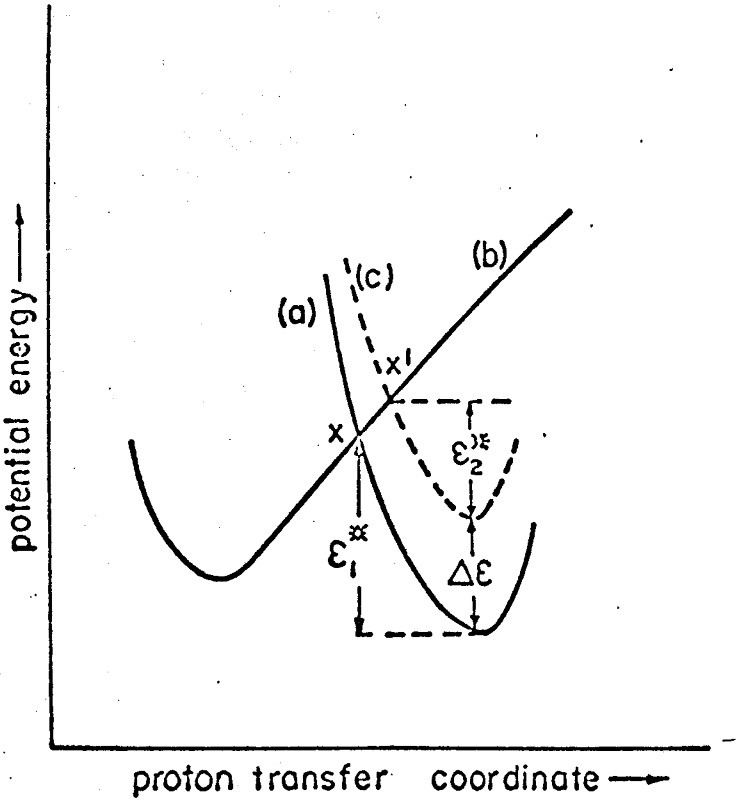

FIG.V,9 Comparison of activation energies for proton and electron transfer

Fig. II,5 - Reproduced from Matthews[75].

> activation energy is ε_1^* in the second it is $(\varepsilon_2^* + \Delta\varepsilon)$, which is clearly greater than ε_1^*. Thus, the path of minimum activation energy corresponds to neutralization of the excited H^+--OH_2 ion by an electron from the energy levels in the metal. Neutralization of an excited H^+--OH_2 ion by an electron from the energy levels in the metal higher than the Fermi level, requires a higher total energy of activation."

Working with qualitative concepts only, Matthews apparently failed to see the physical significance of the above statement. As it will be discussed in section VII,D,5 the higher total energy accounts for the phenomenon of hydrogen overvoltage.

It is clear that, like many previous workers, Matthews, too, committed the common error of disregarding the dynamic nature of the reaction (Time considerations - see review of Butler's work in section II,G,3) and of considering the crossing point X as the equilibrium value for a reversible reaction. This fact is also clear from the way Matthews constructed his graphic interpretation (Fig.II,5). On [75] p. 407 he says --

> "This lead to the contradiction that at the atomic configuration corresponding to the crossing point of the two potential energy curves the species are both charged and uncharged. It is reasonable to suppose that the actual charge on the species in the transition state is neither unity nor zero but somewhere in between. This, however, means that a change in electrical energy $\Delta\phi$, of the initial state causes the electrical energy of the activated state to change by some fraction of $\Delta\phi$. Thus, in addition to the change in energy of the activated state by $\gamma\Delta\phi$ due to the vertical shift of the initial state curve we will have another change $\gamma'\Delta\phi$ due to the existence of a fractional charge..."

He then shows that the average charge of the species is 0.5, thus apparently confusing the concepts of charge of the species z, with the charge transfer coefficient α, in which γ and γ' are already accounted for. (Also, see comments on Hush's work).

It can be seen, therefore, what degree of confusion is introduced if one fails to realize that curve (a) and (c) describe the system prior to the act of electron acceptance by the ion, and curve (b) describes an entirely different system, existing at an entirely different period in time. The only significance of the crossing points X and X' is to determine, on the distance axis, the location of the Electron Plane, as it will be seen in section VI,5.

On [75] p. 409 Matthews states --

> "Application of a cathodic potential difference thus results in a lowering, by $\beta\Delta\phi$ of the amount of chemical energy required to activate the H_3O^+ ion to the configuration, of the activated state".

The misconception involved in the above statement will be discussed in section

On [75] p. 412 --

> "Electrostatic attraction between the proton in the activated state, and the negatively charged electrode will lead to a reduction in the force constant of the symmetric stretching mode."

This is Gurney's approach, which is correct as far as the net results are concerned but leading to misinterpretation when passing from potential energy to energy values.

Matthews gives an interesting distinction between old and recent Double Layer theories. ([75] p. 415) --

> "In the old D.L. theory all the H_2O molecules covering the metal surface could accept a proton from the bulk which then may be discharged at the surface. According to this model, discharge will always occur at the lowest energy metal site and will be independent of electrostriction effects. According to more recent D.L. theory the H_2O are strongly oriented by the surface and do not participate in the bulk water structure through hydrogen bonds. Discharge may then take place only at the remaining free sites. Electrostriction may lead to changes in the dimension of the double layer but will probably not affect the strongly bond H_2O molecules."

In the calculations of the interactions between ions and permanent dipole, Matthews assumes that the dipole moment of a water molecule adsorbed on an electrode surface is 1.85 Debye (from Andersen and Bockris[76]) (1 Debye = 3.33×10^{-30} cm^{-1}), the O-H bond length is 1.50 A, and the double layer width is 1.75 A. This last value is taken from the early works (Parsons and Bockris 1950[57] and, besides being exceedingly small, it is taken as a system parameter instead of being a result of calculation for the electrode process involved. In fact, from [75] p. 450 on, Matthews carries out a trial and error approach to the numerical computation of the rate of reaction, arbitrarily fixing the barrier height, and width, for different temperatures. There is little significance to these calculations.

Matthews' attempt to explain the dependence of the Tafel slope on temperature, meets with difficulties caused by, what Bockris[2] defines as "...orgy of oversimplifications.." The discussion presented in section III,3 provides an approach to the interpretation of this phenomenon.

A very interesting point is made by Matthews ([75] p. 531) concerning the mechanism of impurity effect --

> "Specific adsorption of Cl^- ions will lead to an increase in barrier width. When a Cl^- ion specifically adsorbs on the electrode it attracts the hydrated H_3O^+ whose cation can be discharged. The Cl^- ion has a diameter of 3.62 A compared to 2.76 A for the water molecule. The proton transfer distance thus increases by 0.86 A and the Eckart barrier width increases by about 1.4 A. According to the Bockris-Davanathan-Muller model of the double layer, the neutralized H atom is formed at considerable distance from the electrode where the principal interaction is the $H\text{-}OH_2$ interaction. Increase in the barrier width will thus have little effect on the barrier height or on the activation energy."

However, even in this statement the misconception about activation energies and "barrier heights" is evident.

Very interesting considerations on the effects of a quantal distribution of energy levels on the reaction rate, are given on [75] p. 535.

> "It has been assumed that a Boltzmann distribution of energy levels exists for the initial and final states. The justification for this assumption is as follows: The initial state contains solvated H_3O^+ ion. The H_3O^+ ion has 6 modes of vibration and 2 modes of libration ranging from 2900 to 600 cm^{-1}. In addition, these modes of vibration are perturbed by solvent interaction leading to broad spectral lines. The net effect is the formation of a quantized but overlapping, and hence approximately continuous, distribution of energy levels. The final state contains M-H and H_2O. The M-H

> molecule has only one mode of vibration and hence a quantal distribution exists. The H_2O molecule has 3 modes of vibration and 2 modes of libration. Thus although the M-H levels are quantized, the levels of the final state are approximately continuously distributed due to the thermal distribution of the energy of the H_2O molecule."

Matthews mentions several authors who have applied corrections to the above model, and found little effect on the validity of the assumption. Along the same lines of reasoning he introduces another very interesting idea --

> "The assumption that the energy levels are not quantized to any significant extent is confirmed by the Tafel plot. Thus, if the energy levels of the initial state were quantized, then, in the absence of tunneling, one would observe steps of constant current, each step extending $2(\Delta E)F$ Volt, where ΔE is the distance between quantized energy levels. Thus, for proton discharge one should observe steps 650 mV apart if the initial state were quantized with respect to the $H_2O{-}{-}H^+$ stretching vibration. Such a degree of quantization would be prohibitive to proton tunneling, since the chance of matching the quantum levels on either side of the barrier would be very small. The fact that we observe linear Tafel lines is thus considered evidence for an approximately continuous energy level distribution. The fact that one sometimes observes a rather sinusoidal scatter of points about the linear Tafel line, may, however be ascribed to the effects of a quantal distribution 'dampened' by proton tunneling."

Referring to the probability of tunneling, Matthews indicates ([75] p. 542) --

> "With increase in cathodic potential, the width of the barrier to electron transfer increases and hence the tunneling probability decreases."

Therefore, the assumption made for the electrodynamic model, which eliminates the contribution of tunneling appears to be correct.

Regarding the width of the barrier Matthews states on ([75] p. 537) --

> "The present results of the most probably barrier width, 4.0 A is equivalent to a proton transfer distance of 3.7 A between the metal surface and the center of the oxygen of the discharging proton".

Two important considerations are given on [75] p. 544 --

> "From the standpoint of electrocatalysis it is important to adjust conditions such that the barrier width is a minimum, e.g., by replacing the electrode water molecules by smaller molecules or by preventing the breakup of the solvent structure. From the viewpoint of corrosion, it is necessary to increase the barrier width, e.g., by replacing the electrode water molecules by larger molecules."

The electrodynamic model can offer a quantitative evaluation of the above phenomena and hence provide a means of predicting the effect of certain molecules on electrocatalysis or corrosion.

Matthews admits that

> "The theory which relates the symmetry factor to the slopes of the initial and final state potential curves has a serious deficiency. According to the method a change of potential by $\Delta\phi$ causes a vertical shift of one curve, e.g., for the discharge reaction the final state is held fixed and the initial state curve shifted by $\Delta\phi$. Each nuclear configuration $M\text{-}e^- + H^+\text{-}OH_2$ receives an energy increment of $\Delta\ \phi$..."

However, it should be realized that the energy increment may be less than $\Delta\phi$ because of the value of the charge transfer coefficient. Furthermore, the Bockris definition of the symmetry factor[2]

$$\beta = \frac{\text{Distance along the reaction coordinate between initial and activated state}}{\text{Distance along the reaction coordinate between initial and final state}}$$

is not sufficient for its determination. Matthews continues --

> "...The most important single quantity in electrode kinetics is the symmetry factor, for without β electrode kinetics reduces to heterogenous chemical kinetics..."

This is correct, as can be seen from the Absolute Reaction Rate:

$$K_r = K\,\tau\,e_o\,(kT/h)\exp(-\Delta G_o^{+}/RT)\ \exp(-\beta\ nF\Delta\phi_{rev}/RT)$$
$$\exp(-\beta\ nF\eta/RT)$$

where:

K = classical transmission coefficient

τ = quantum mechanics transmission coefficient

n = number of charges transferred

For β = 0, the above expression reduces to a chemical rate equation.

In the conclusion of his work Matthews states --

> "...The experimental inability to obtain a constant α [*chemical charge transmission coefficient*] at all temperatures is paralleled by the theoretical inability to adequately explain why β is constant over such wide range of potential and why β = 0.5 for such a wide variety of electrode reactions. In theoretical discussion of β the dependence of both the resonance lowering of the energy of the crossing point and the zero point energy of the activated state on potential have been neglected. At high current density the inapplicability of the equilibrium assumption between initial and activated states will break down, yet linear Tafel lines are observed even at these high current densities.
>
> The very foundation of the electrode kinetics is weak, necessitating intensive research."

In summary, Matthews' work can be considered a very comprehensive review not only of the hydrogen evolution reaction but also of the present state of electrochemical kinetics.

Kuhn et al.[77] give modern (1971) data for correlations between the rate of hydrogen reaction and the physical properties of the metals, which do not contradict the trend of Matthews' conclusions, but tells us to be --

> "...cautioned against correlations without strong theoretical justification, since virtually all physical parameters show a periodic variation with atomic number and hence will be expected to correlate with each other..."

This section will be concluded by noticing that Krishtalik[78] also in his continuation of Frumkin's[79,80] work on hydrogen overvoltage, developed a position much closer to the Levich, Kutznetsov, Dogonadze approach. This is another indication of that the correct way of approaching the study of electrode processes is by the combined mechanism of electron and ion transfer.

K. METAL PHYSICISTS VIEW AND DIELECTRIC COEFFICIENT OF INTERPHASE

Mott and Watts-Tobin[81] present the metal physicists view of metal/electrolyte interface. Their revival of Rice's model for the penetration of the electric field into the metal, and their treatment of the behavior of a thin film of water in a strong electric field, are important for the development of the electrodynamic model, and some comments to this effect are given below.

O.K. Rice[82] was the first (1928) to suggest that the electric field would penetrate into the metal. The electric field strength at a distance x from the surface, inward into the metal is

$$F = E_o \exp(-x/b)$$

where:

E_o electric field strength outside the metal (in vacuum)

b $[(h^2/4me^2)\ (3N_o/\pi)^{1/3}]^{1/2}$ which, according to Mott and Watts-Tobin's analysis, based on the Thomas-Fermi method gives: $b \sim 0.5$ A

N_o number of (free) electrons per unit volume in the metal.

This penetration contributes a term $1/4\pi b$ to the capacitance in a series with that of the electrolyte side of the interface. Fig. II,6a shows the field as a function of distance at the interface between a metal and a vacuum, and Fig. II,6b shows how it might look according to simple electrostatics at the interface between a metal and water.

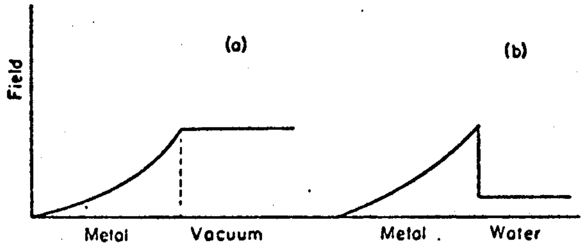

Fig. II,6 - Reproduced from Mott and Watts-Tobin[81].

Rice's model explains nicely the roughly constant capacitance, independent of cation type, that one obtains in the cathodic side of the capacity versus potential curve. Rice's model has not been accepted chiefly because the capacitance of the interface at a mercury electrode appears to increase indefinitely for increasing anodic potential, and this is not compatible with a capacitance $1/4\pi b$ in series. Mott and Watts-Tobin show that this criticism is not valid for fluoride solutions, in which specific adsorption is absent, and the anodic rate of increase is independent of fluoride ion concentration, but temperature sensitive. Moreover, the cathodic rate of increase is independent of temperature, cation type and concentration.

However, Mott and Watts-Tobin consider Rice's model quantitatively wrong, because the field does not jump sharply at the interface from $4\pi\sigma/\kappa$ in the water side to $4\pi\sigma$ in the metal where there is no water (σ the charge, κ water dielectric constant). Mott and Watts-Tobin explain that the above transition requires a distance greater than b, and the dielectric constant within the Helmholtz layer must be lower than that for water.

We will see in the discussion of the Electron Surface how it is easier to explain the behavior of the capacity versus externally applied electron potential difference curve, in terms of the electrodynamic model, where the potential shifts the location of the electron surface thus determining the local volume charge density. Mott and Watts-Tobin's view of the charge transfer coefficient is based on the adatom-kink sites mechanism. Nevertheless they developed a tentative analysis from which, as an interesting result, α_c comes out to be less than 0.5; while for dissolution, in which the nucleation process is the creation of a hole in the surface layer (and thus results in a dipole in the opposite sense), α_a should be greater than unity.

On the behavior of a thin film of water in a strong electric field Mott and Watts-Tobin note that double layer theories treat the dielectric as a continuum, neglecting the discreteness of the charge effects; water is then taken as a medium with its normal dielectric constant ($\kappa \sim 80$). This is not correct when, for example, cations are present in the double layer. Around these cations the water will be strongly polarized by their field -- the polarization will reach saturation for water molecules which are nearest neighbors -- so the dielectric constant will be no longer as large.

Further, Mott and Watts-Tobin recall that the high dielectric constant of water in the bulk is largely due to the correlation between the directions of the dipole movements of neighboring molecules produced by their hydrogen bonds. This correlation is much less in a thin film of water of dimension given by double layer theories. Moreover, for water molecules that are nearest neighbors to the metal atoms of the electrode surface, only one component of the dipole moment of the molecules can be reversed by the electric field, the remainder of the moment being tied down by the neighboring metal atom. This reduces the effective dielectric constant of water in the double layer still further. If the dielectric constant were to reach its full normal value of 80, the capacity would be about ten times greater at the electrocapillarity maximum than actually observed. We see that these considerations are very useful for understanding the composition, that is, which entities and in what state are to be found within the electronation interphase.

The electric field strength is also regarded as constant throughout the double layer by the above theories. Mott and Watts-Tobin point out that this is the case only when no ions are present in the double layer. The lines of force will leave the negative charge in the metal, and continue across the double layer until they terminate on charges in the electrolyte. However, when ions are present in the double layer, the value of electric field strength cannot be regarded as constant throughout. In fact, the lines of force will not penetrate into the electrolyte, but will terminate on charges in the double layer. Mott and Watts-Tobin are among the very few authors who explicitly mentioned the order of magnitude of the electric field strength across the metal-electrolyte interface when an externally applied potential difference of 0.5 V is superimposed:

$$(F \sim 10^7 \ V/cm)$$

The existence of electric field strength of this magnitude is one of the bases for the electrodynamic model.

Subsequently, Bockris' group[83,84] developed a molecular approach to estimate the combined influences of localized ionic fields and that of the electrode in relation to hydration effects. This theory, which is referred to in the literature as BDM (Bockris, Devanathan, Muller) provides quantitative details for the role of the solvent orientation and specific values of the dielectric coefficient (as low as 5.3) for certain regions of the solution side of charged interfaces.

Very recently Barradas and Sedlak[85] improved on the BDM theory with emphasis on the temperature dependence of the dielectric coefficient of the solution interphase, which, they state -- reflects the confluent nature of macroscopic and microscopic fields operating at the solution interphase -- where -- the solvent molecules are subjected to competitive or reinforcing influence of the fields arising simultaneously from the polarization of the electrode and those due to the ions in the double layer. They distinguish between macroscopic field effects associated with the existence of a finite charge density q, on the metal surface (for which they define q=0 as the point of zero macroscopic coulombic surface charge density) and microscopic fields with localized ion-solvent interactions in the interphase. In their characterization of the interphase structure, x_f is the thickness of an ion-free layer of solvent molecules on the electrode surface, which is taken to be 2.8 Å (the diameter of a water molecule), and x_d is the thickness of a region extending into the solution beyond 2.8 Å, which is anisotropic because of the presence of ions and solvent molecules. Beyond the distance $d=x_f+x_d$ is the region of bulk properties. Barradas and Sedlak propose the following expression for the calculation of x_d in Angström as a function of ionic strength I, in g-ion/liter, dimensionless dielectric coefficient of the interphase ε, and absolute temperature T:

$$x_d = 0.3368\ [(\varepsilon/I)\ (T/298)]^{1/2}$$

This is one of the few published expressions of its kind in which the temperature is a variable. However, although these authors were careful to stress ε for the interphase, rather than that for the bulk, should be used, they failed to use T of the interphase and used the bulk temperature instead.

Barradas and Sedlak also found that the dielectric coefficient for various non-specifically adsorbed electrolytes decreases with increasing ionic strength leveling off at about 11. In this regard they made a very interesting observation --

> "It is not unreasonable to assume that at an ionic strength approaching the solubility limit of electrolytes, the structure of the double layer may approximate to that of an ionic melt."

This is in agreement with views expressed in a previous work.[86]

Regarding the effect of the electric field strength on the value of dielectric coefficient for water, these authors compiled the existing data showing a decrease with increasing field strength above the 10^5V/cm value, up to 10^7V/cm beyond which it is not too clear from their graph ([85] Fig.4) if the limiting value would drop below 10.

Finally, their treatment of the temperature dependence of ε is based on Frohlich's theory of the static dielectric coefficient of a dipolar solid, and they stressed Frohlich treatment on similarities of dielectric behavior of disordered solids and of liquids. Incidentally, in a very recent work on paracrystalline structure of molten metals, Hosemann et al. [87] gives radial density functions out to a distance of 25 Å, and the melt is described in terms of fcc lattice, with a lifetime of about 10^{-11} s. These observations are important in the description of the nature of the metal electrode/ electrolyte interphase of the electrodynamic model. Barradas and Sedlak give the following description of the dielectric coefficient variation with temperature --

- ε has a minimum value at 0°K which is larger than the Maxwellian limiting value which correspond to the square of the refractive index;
- as the temperature increases, ε increases according to a relation which includes the average energy difference between two equilibrium orientations of the dipolar solid;
- at a certain temperature T_c, just below the melting point of the solid, an order-disorder transition occurs, after which ε decreases with temperature, for $T > T_c$;
- extrapolation to an infinite temperature would result in a limiting value of the dielectric coefficient which would be free from contributions due to permanent dipole moments.

For 0.795 M aqueous NaF, which is comparable with BDM's ε_L value of 5.3, these authors report a value of 4.6 for ε.

In this context one may wonder if the so-called "Polarization Catastrophe" is really a contradiction. Eyring et al. [88] used the Clausius-Mossotti formula with Lorentz expression for the local field and found the high frequency dielectric coefficient to be infinite at a certain T_o. They estimated the order of magnitude for T_o to be 10^3 °K -- For $T > T_o$, ε decreases and for $T < T_o$, ε is negative.

If one uses their treatment and assumes $T_o = 1{,}800$°K, the curve reproduced in Fig.II,7 results. We see that in agreement with Barradas and Sedlak[85] there is a major discontinuity (from $-\infty$ to $+\infty$) at T_o which happens to be in the temperature region of the melting point of most metals.

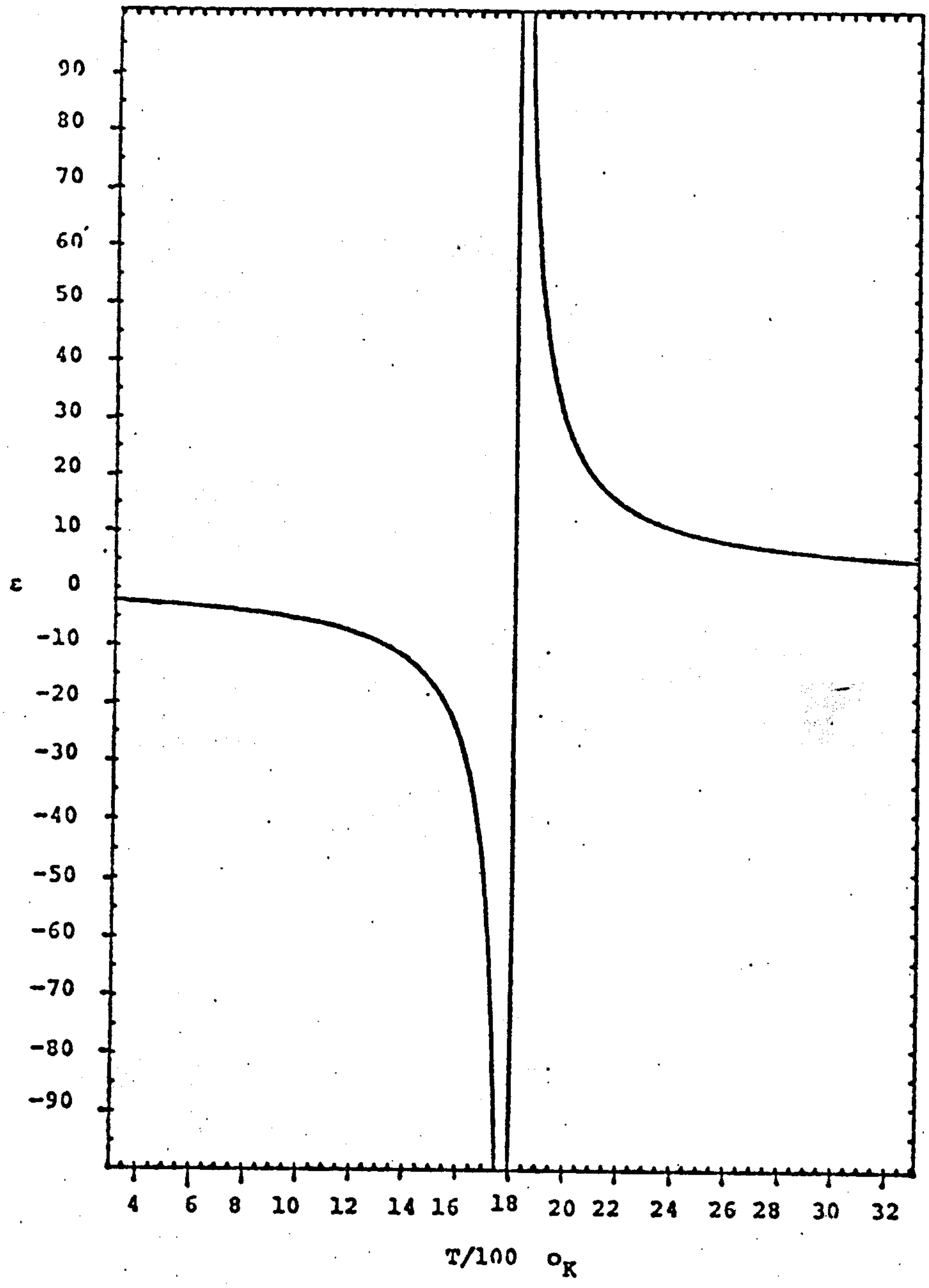

Fig. II,7 - Eyring's et al.[88] 'polarization catastrophe'.

The above considerations are of great importance for the construction of the electrodynamic model.

Negative values of Dielectric Constant are not uncommon for metals; as reported by Mott and Jones[89], the value for silver calculated from the optical constants of the metal is -2. McIntyre[90] reports and has used values as low as -15. We will see the results of the effect of the value of the dielectric constant on the potential energy of electron extraction curve in section VI,D.

L. THERMODYNAMICS OF ION HYDRATION

1. Structure of Aqueous Electrolytic Solutions

The region of the interphase where the electrolyte properties approximate the bulk, is the solution side boundary for this investigation. Therefore the structure of the bulk liquid medium will be only briefly mentioned.

The most commonly used liquid medium (solvent) for the electrode processes is water, which is, in Horne's[91] words --

> "The most extraordinary and complex substance known to men, anomalous in all of its physical-chemical properties. The structure of liquid water is not known. There are very many different theories of water structure, and the confusion in the literature is great; not because these theories fail, but because many of them work suprisingly well. The failure of modern techniques, techniques powerful enough to resolve the structure of such exceedingly complicated biomolecules as DNA and myoglobin, to disclose the structure of water, give us due warning that we are dealing with a system of horrendus complexity."

Desnoyers and Jolicoer[93], in thier comprehensive review of thermodynamics of ion hydration, give some insight on that complex and controversial subject by saying that -- since hydrogen bonds are being broken and reformed continuously due to thermal motion, each physico-chemical property of water may give a different insight into the local structure, according to the time scale of the observation and the averaging process over the bulk. They propose that, since we are interested in the changes in the structure of water by the presence of the solute, these changes can be treated, at least qualitatively, without an actual final knowledge of the absolute structure of water.

In the light of the above considerations, throughout this thesis, water will be regarded as having a dynamically stable structure, with hydrogen bonds and electron arms which can adjust for a large number of different structures.

2. Hydrated Ions

Regarding the quantitative treatment of hydration, there is strong disagreement among authors, because the water molecules are in continuous exchange with the water in the bulk of the solution. Only in a time average it may be said that a hydration shell exists around most ions. At finite concentrations, besides ion-solvent interactions, we have long-range coulombic forces (up to 200 Å, according to Adamczewski) between ions, and short-range Van der Waals forces, for which Desnoyers and Jolicoeur say that the solution begins to resemble the state of a molten salt. At 3-4 molal, just enough solvent molecules are there to surround the ions; hence we have a solution structure which is completely different from the dilute solution models.

Bockris[2] proposed a definition of primary hydration shell which comprises a number of water molecules immobilized by the ion and moving as one entity with it. But this is true only in the case of what Desnoyers and Jolicouer[93] call, hydrophilic hydration, as opposed to hydrophobic hydration occurring when non-polar groups act as fifth coordination neighbors to the tetrahydrogen-bonded water molecule and occupy space that would normally be free space in pure liquid water. This brings us in the far reaching problem of the division of ions into structure makers, or order formers, and structure breakers, depending on what type of hydration predominates.

Samoilov[94] introduced the interesting notion of negative hydration considering the water's dynamic state. He states that a water molecule close only to other water molecules may remain in its equilibrium position for an average time τ. If an ion is brought into the neighborhood of a water molecule, its time of residence in the equilibrium position will no longer be equal to τ since an ion and a water molecule are not energetically equivalent -- let this average time be τ_i. The fact that $\tau \neq \tau_i$, essentially depends on the alteration of the height of the potential barrier opposing exchange of the nearest water molecule under the influence of the ion. Thus, the ratio of the two times is shown to give a quantitative estimate of energy of hydration. These τ are on the order of 10^{-9} s, and the frequency of vibration of a water molecule about its equilibrium position is assumed to be independent on whether this position is close to or far from the ion.

The ions for which $\tau_i < \tau$, and which cause the water molecules in its vicinity to undergo more frequent exchange with other water molecules, are said to undergo negative hydration. These are large ions with single charge. The opposite phenomenon is observed for small multiple charged ions, which diminish this motion of exchange. This concept is related to the negative viscosity as treated by Frank, Evans and Gurney.

3. Hydration Number

Since ions and water molecules are not energetically equivalent, a number of molecules of water are required to establish a dynamic equilibrium with an ion. The survey for ionic hydration numbers led to an embarrassing scatter of values for which it was impossible to obtain a reasonable correlation for the various ions. The various authors gave a different meaning to the idea of hydration number and measured it with different methods. Among these, Sukhotin and Kazankina[95] recently presented what is possibly the definition most appropriate for this investigation. The translational ionic hydration coefficient is defined as the number of water molecules transported by the individual ion during translational movement in an electric field. Unfortunately, they only describe the technique used to measure the volume changes of a membrane bonded central compartment, of an electrolytic cell, without giving the results; possibly saved for future papers. One is therefore obliged to use some arbitrary procedure for estimating this energetically important parameter.

4. Hydration Energy

Considerable data is available in the literature regarding enthalpy of hydration, and Basolo and Pearson[96] offer a compilation of most of them. However, a meaningful ordering of these values in a sequence correlating to some property of the metal ions is not possible, since they are very similar mostly falling in the range, 450-500 kcal per mole.

The methods available for the evaluation of ionic enthalpies of solvation have been recently reviewed by Somsen, Weeda[97] and Los[98]. Their comparison of Born-Bjerrum's continuum model versus Buckingham's discontinuous molecular model show that the splitting procedure for individual ions values according to the discontinuous approach is superior.

On the contrary, very little is published about entropy of hydration and consequently on free energy of hydration, for conditions other than infinite dilute solutions. In a recent work Chernomorskii[99] gives a summary of this category of data and points out the following very interesting correlations for amalgams and solid metal electrodes:

- the value of the exchange current decreases for increasing values of entropy of hydration;
- the value of the overpotential (at the same current density) increases for increasing values of entropy of hydration.

Consequently, he stresses that the energy of hydration, which characterizes the energy state of the cation in solution, does not fully correspond to the kinetic hindrance in the reorganization of the hydration shell during discharge-ionization reactions. Instead, the entropy of hydration of ions linearly depends on cation effective potentials $\frac{z}{R}$, where z is the charge of the ion and R its radius. Thus, it is the hydration entropy which is related to the degree of polarization of the medium by the ion and reflects the arrangement of the solvent resulting from hydration.

Chernomorskii concludes by saying that the kinetic hindrance in the rearrangement of the hydration shell of cation during their discharge-ionization reactions, depends not only on the degree of the hydration, but also on the character of the reaction of cations with the electrode metal. The above statement is in agreement with the concepts on which the electrodynamic model is based, and these results are explained by Eastman's entropy theory, even though his work was published before the concept of exchange current was established (see sections II,F and II,I).

It is therefore regarded as appropriate to reproduce portions of Eastman's paper[165c] in which he describes the nature of heats of transfer in solutions of electrolytes --

> "For the purpose of the present discussion the space in the vicinity of an ion in an undissociated polar solvent may be divided, roughly, into three concentric regions of gradually differing properties. First, there is the 'ion-cavity', within which there are no solvent molecules. This space varies in size from case to case and appears to be large compared to the volumes defined by the outer electron orbits of

> the ion. Immediately outside of the ion cavity the (polar) molecules of solvent are strongly attracted and oriented. The inner layers of solvent molecules in this second region, and those extending out from it to varying distances in different cases, are held so strongly by the central ion as to form a complex with it, acting in process of diffusion, as a single molecule. The third region comprises all the rest of the outer space. In this sphere the solvent molecules are still subject to forces of compression and orientation, diminishing with distance from the center of the complex, and not sufficiently strong to bind these molecules to the ion. The second and third of these regions obviously merge into each other in such a way as to prevent sharp boundaries from being drawn between them.
>
> When a solvated ion of the kind described is transferred by diffusion from one region to another of the solvent, the aggregate comprising the first and second regions above remains mostly intact and takes part in no internal energy or entropy changes. But as the ion moves it leaves behind material which had been under its influence in the third sphere, and brings under its influence solvent molecules not previously so strongly affected. A relaxation occurs, therefore, in the region from which it goes [*away from*], with an attendant increase in entropy and absorption of heat. The reverse effects appear in the region into which it moves."

These types of considerations, as has been already indicated in section II,F, are of great importance for the development of the electrodynamic model. Eastman then continues --

> "The possibility that either ion of the solvent may be transferred, in effect, by a chain mechanism must also be considered in solutions of acids and bases. For if this occurs, not only the energy represented in the third sphere above, but that of the second as well, a very much larger quantity, would be involved in the heat of transfer."

The seeds of a development similar to the electrodynamic model can be seen in the following suggestion --

> "The simple mechanism pictured above would appear to afford a basis for quantitative theoretical treatment. The entropy effects in region three about the ion depend upon the degree of compression and orientation of the solvent molecules in it. Both are approximately calculable in any element of volume at a given distance from an ionic center by methods like those of Webb. The dependence of the entropy of the solvent upon pressure is measurable, and the entropy change due to orientation might be calculated from the relative probabilities of the axial distributions of the dipoles in the field of the ion and without it by methods like those of Langevin. Volume integrations throughout the sphere should result in the desired entropy. One of the limits of the integration is obviously infinity. The other, which is the boundary between regions two and three, is somewhat indefinite and variable from one ion to another. It could probably be fixed with enough exactness as the radius at which the equipartition amount of kinetic energy would be just sufficient to carry a solvent molecule against the force of attraction of the ion (known as a function of distance) to infinity. This would be, on the average, the dividing line between the 'bound' and 'unbound' solvent molecules, and would serve to define the third region above for the purpose of integration. The calculation outlined therefore appears theoretically feasible."

The aim of the analytical part of this thesis is precisely to attempt these types of calculations.

M. ELECTRIC FIELD EFFECTS ON ELECTRODE/ELECTROLYTE INTERPHASE

1. Introduction

This aspect of the electrode process is dealt with mostly by physicists, who view the ion hydration complex in the light of electrodynamics and for which Sommerfeld's[102] treatment is regarded as the fundamental source for concepts and definitions.

A comprehensive review on ionization, conductivity and breakdown in dielectric liquids has been recently presented by Adamczewski[103]. He recalled the theory and mechanisms of conduction for low and high fields from Onsager, Plumley to the latest treatment of his own.

The field is usually considered uniform and normal to the electrode surface. However, the possibility of non-uniformities at various points of the electrode/electrolyte interphase must be considered.

Treier and Borovkov[104], in connection with the development of electrochemical cells as controllable memory devices, reviewed the methods for calculating the distribution of the current and of the potential over the electrode surfaces. In view of the complexity of the analytical solutions they concentrated on graphical methods which account for the resistance of the electrodes and for the polarization of electrode surfaces.

Recently, Ivanov[105a] has proposed an approximate analytical solution for the current and potential distribution in a cell with rectangular geometry, accounting for the enhancing or hindering effects of electrode polarization on current uniformity. In an earlier work[105b], this author has evaluated, using numerical methods, the non-uniformity caused by evolution of gas bubbles and variation of electrolyte gas content.

2. The Wien Effect

As it has been seen on reviewing Mott's and Watts-Tobin's work, the electric field strength across the electrolyte/electrode interphase is very high, in the order of magnitude of 10^{10} V m^{-1}, for electrode processes under practical industrial conditions. Therefore, in considering the state of the species which are contained in the interphase it is necessary to realize that in the presence of such an electric field strength, these species will certainly behave in a way different from that of bulk electrolytic solution under low fields, and for which Ohm's law applies (i.e., the velocity of migration is independent of the strength of the applied field). This is in fact what Wien discovered in 1927 -- namely that at a field strength above 10^6 V m^{-1}, the conductivity of a strong electrolyte increases with increasing field strength. This is usually called first or normal Wien effect; the second being related to an increase in the degree of dissociation of weak electrolytes under high field.

What is surprising is the fact that this phenomenon is seldom mentioned in electrochemistry treatises (Kortum[173] is the exception among the few). To obtain a complete review of this effect and information regarding its explanation one has to go back to the work of Eckstrom and Schmelzer[106] in 1939.

The qualitative understanding of the Wien effect can be summarized as follows:

-- at electric field strength approaching 10^6 V m^{-1} the ion velocity in the course of its oscillations relative to its water molecules of hydration, becomes so high that the distance travelled by the ion, within the water relaxation time is of the same order of the radius of the ionic atmosphere. It follows that the ionic atmosphere cannot be maintained any more and the ion acquires a linear velocity of the order of meters per second.

If we recall that the ions in the bulk of the electrolyte have drift velocity of the order of 10^{-6} m s^{-1} in a field strength within the bulk of 1. V cm^{-1}, which is on the high region for industrial cells, it is not difficult to recognize the importance of the Wien effect on the de-hydration step of metal deposition electrode process.

The above mechanism plays an important role in the electrodynamic model.

In a very recent work on electrohydrodynamics of certain homeotropic nematic liquid crystals, Penz and Ford[107] described a very interesting phenomenon. When subjected to d-c electric fields parallel to the nematic direction, the liquid breaks up into a series of cylindrical lenses above a certain voltage. This work may be applied to aqueous solution to give information on the magnitude of the two dimensional distortions acting on polar molecules subjected to high fields, and on the motion mode initiated by these molecules to relieve the stress.

3. Pressure

Another electric field effect for which surprisingly, little work exists in the literature, is the pressure in the interphase generated by the electric field itself.

As early as 1954, Macdonald[108] published values of 3,000. atm acting in the interphase when a field strength of the order of 10^9 V m^{-1} existed inside the interphase, and, most interestingly, this pressure was associated with a 20% compression.

More recently, Macdonald and Barlow[109] proposed a theoretical development for calculating the electrostatic pressure from electrostatic energy which combines compression, electrostriction and dielectric saturation, resulting in pressure values even larger (6,000. atm) than the previous work.

In a very recent work, Sato[8] reports to have calculated electrostriction pressures, on an anodic film, larger than 1,000. atm. He, however, does not mention the method used to determine this value.

4. Hydrated Electrons

Adamczewski[103] reported that at the beginning of the last decade Weiss proposed the use of the polaron theory to explain the mechanism of water ionization, assuming the existance, in the case of the negative polaron, of a complex formed by an electron orbiting a water molecule and surrounded by a shell of water molecules polarized by it. Weiss proposed an expression for calculating the radius of a negative polaron which comes out to be 10 Å, and its lifetime was estimated to be 10^{-9} s. Hart and Boag[111], about ten years ago, were the first to experimentally demonstrate the existence of negative polarons in water by way of radiolysis experiments. Soon after, the above concept was applied and developed in electrochemistry under the name of hydrated electron, e^-_{aq}. The latest comprehensive review works on the subject are offered by Kenney and Walker[112] and by Conway[113]. These authors show that hydrated electrons are ordinary chemical entities to which reaction rate parameters (activation energy), diffusion coefficient (5×10^{-5} cm^2 s^{-1}) effective collision diameter (6 Å), hydration energy (40. Kcal mol^{-1}) can be assigned. Only the position of the electron cannot be located with precision greater than a few Ångströms, because of its small momentum when in thermal equilibrium with its solvent at about 300°K, by consideration of the Heisenberg uncertainty principle.

The rate of reaction of e^-_{aq} with its solvent water molecules is very slow:

$$k = 16M^{-1}\ s^{-1} \quad \text{for:} \quad e^-_{aq} + H_2O \rightarrow H + OH^-_{aq}$$

thus, it cannot be dismissed as a transient species of little importance.

The above reaction is used to calculate the thermodynamic properties of e^-_{aq} including its standard potential (-2.7 V). The reason why the hydrated electron was not detected before is primarily because it cannot exist in concentration higher than 10^{-4} molar due to the reaction:

$$e^-_{aq} + e^-_{aq} \rightarrow (e^=_2)_{aq} \rightarrow H_2 + 2OH^- \text{ with } k = 0.5\text{x}10^{10}M^{-1}\text{sec}^{-1}$$

For electrolysis, Kenney and Walker tentatively suggest, that if one gram mole of hydrated electrons could be generated at the electrode by the passage of a Faraday of charge, then, in order to produce 10^{-4} molar of hydrated electrons within a layer 1,000 Å thick at the electrode surface, we would need a current density of 50 mA cm^{-2}. Since the mean lifetime of e^-_{aq} at 10^{-4} molar would be about 1 μs, it is impossible to obtain a layer thicker than 1,000 Å because this is the maximum distance, e^-_{aq} could diffuse in 1 μs, with the diffusion coefficient given above, and the electric field strength beyond the double layer could not sustain a significant mobility.

Finally, Kenney and Walker[112] speculate on a most interesting work by Yurkov[114] on colloidal copper reduction at macrodistances from the cathode. They suggest that this phenomenon occurs because of the action of dielectron species $(e_2^=)_{aq}$ which is the product of two hydrated electrons formed at the cathode. This dielectron species might have a sufficient lifetime to migrate toward the incoming Cu^{++} and initiate the neutralization at some distance from the electrode surface. Yurkov reported distances up to 1. mm when 2. V were applied to Cu refining cell thereby having very high current densities $\approx$ 2. A cm^{-2}.

In summary, if we can postulate that hydrated electrons will be formed in water adjacent to a cathode which is made to eject electrons by suitably adjusting its electric potential with respect to the water, it is like suggesting that the Fermi levels of metallic electrons are significantly affected by the presence of water, and that the work function value should be substantially lower than its value in the vacuum. These observations will be used in the development of the electrodynamic model.

N. THE WORK FUNCTION

Precise methods for determining work functions values for metal/solution interphases do not seem to have been completely established as yet. The error involved in using work function values determined for metal/vacuum systems, in electrochemical processes, seems, at least on first consideration, to be quite significant. Besides, there are various methods for determining these metal/vacuum values and also different values of work function are experimentally obtained under different conditions. For example, the theory of thermoionic emission was used by Matthews[75], as reviewed in section II,J, when it is known[161] that at the electrode solution interphase, in most instances, we have only cold field emission because the local electric field strength is larger than $10^8 V\ m^{-1}$. Nevertheless, the phenomenon of galvanoluminescence indicates the existence, in some cases, of photoemission; thus, the photoelectric work function values may be appropriate.

Recently Trasatti[162] presented a very comprehensive treatment on the subject of the work function, compiling most of the available data. Through successive correlations of work function "physical" data, with potentials of zero charge, and Pauling chemical electronegativity data, Trasatti determined the values of "electrochemical" work functions and values for "effective" electronegativities.

His electrochemical value for copper is 4.7 eV, which is higher than those found in the literature, where the values range from 4.35 to 4.55 eV. However, for platinum, the "electrochemical" value of 5.03 eV is lower than the "physical" value which ranges from 5.20 to 5.40 eV. It should be noted that in his calculations, Trasatti used a dielectric constant value of 7.5, a water projected area of 1.23 $\mathring{A}^2$, and a standard chemical free energy for the hydration of the proton of -263 kcal mol^{-1}.

Toward the conclusion of his work, Trasatti offers a very interesting suggestion -- metals with high work functions have a large electron density in the surface layer, and this would favor strong interaction with hydrogen atoms. Instead, metals with low work functions possess electrons with low kinetic energy in the Fermi level, and this would favor a large interaction with oxygen.

Moreover, he acknowledges that in the literature it has been suggested that water is adsorbed on transition metals through a water dissociation reaction, with the OH group still lowering the work function of the metal; which in the case of iron amounts to approximately 1. eV. He points out, however, that when this occurs, a charge transfer process takes place and the metal cannot be considered to remain at the potential of zero charge.

On this subject, Wells and Fort[163] very recently proved that for aluminum, water vapor does not lower the work function, but oxygen at low pressures (10^{-8} - 10^{-6} torr) does for temperatures above 25°C (-0.25 eV at 200°C, and larger decreases at higher temperatures). The most interesting result they present is the increase in the value of work function produced by oxygen at -30°C; this may prove to be a partial explanation for the low efficiency of the oxygen electrode, which will be discussed in section II,Q,5 At higher pressures (10^{-3} - 10 torr) oxygen increases the value of the work function. Wells and Fort interpreted their results in the following way -- oxygen adsorption on the outer surface of the metal increases the work function, whereas when it is chemisorbed it forms a structure lower work function. In addition oxygen forming oxides increases the work function while the whole process is a function of oxygen pressure and temperature.

Larger decreases in work function are reported by Gesell and Arakawa[164] for magnesium and oxygen, from 3.3 - 1.8 eV.

In order to more precisely define the relevance of the work function value on electrochemical processes, it is appropriate to review the very recent work by Bockris, McHardy and Sen[156] in which they show that for simple non-bonding electron-transfer reactions, no effect of the electrode material is to be expected, since the net contribution of the work function to the cell e.m.f. is zero. Having described the work function for the case of an isolated uncharged phase, these authors then state --

"In a charged phase, e.g., an electrode in contact with a solution, the chemical potential μ_e [*of a single electron*] must be replaced by the electrochemical potential $\tilde{\mu}_e$, i.e., the Fermi level is equivalent to the electrochemical potential of a single electron:

$$E_f = \tilde{\mu}_e/N \tag{9}$$

By introducing the concept of the inner electrostatic porential in the metal ϕ^M, $\tilde{\mu}_e$ may be formally separated into chemical and electrochemical components:

$$\tilde{\mu}_e = \mu_e - F\phi^M \tag{10}$$

the negative sign resulting from the negative charge of the electron, [*F is the Faraday constant*]. No effect of the electrode material is anticipated for simple electron transfer (non-bonding) reactions for the following reasons. Consider the redox reaction:

$$A^Z + e \rightleftarrows A^{Z-1}. \tag{11}$$

At equilibrium, i.e., at the thermodynamic reversible potential, the electrochemical potentials of reactants and products respectively are equal:

$$\tilde{\mu}_Z + \tilde{\mu}_e = \tilde{\mu}_{Z-1}. \tag{12}$$

Neither $\tilde{\mu}_Z$ nor $\tilde{\mu}_{Z-1}$ can depend on the electrode [*inert conductor*]; therefore $\tilde{\mu}_e$, which is the molar equivalent of the Fermi level, (Eq. (9)) must be the same for all electrode materials:

$$\mu_e - F\phi^M = \text{constant.}$$

At first sight, this conclusion is paradoxical because the value of ϕ^M, since it must compensate for μ_e, will vary from one electrode material to another, and might be expected to produce variations in the cell E.M.F. - a thermodynamic impossibility. The paradox is resolved by considering the metal-metal junction between working and reference electrodes. The effect of ϕ^M on the p.d. [*potential difference*] at the junction will be equal and opposite to its effect on the p.d. at the metal solution interface[*s*]. The net

> contribution of ϕ^M to the cell EMF is thus zero. The preceeding discussion concerned an electrode only at the reversible potential, but the conclusions are equally valid at any given potential. If comparisons were made at a potential η volts below the reversible potential, the inner potential of the electrode would be lowered by η volts and the new (molar) Fermi level would be:
>
> $$\tilde{\mu}_e = \text{constant} + F\eta,$$
>
> which would still be the same for all electrode materials."

It is clear that the above treatment applies only if the electrode processes are isothermal. For the case of non-isothermal behavior of irreversible electrode reactions (upon application of an overpotential), the metal-solution interphases of the two electrodes will have temperatures different from each other and from that of the cell. Therefore, the metal-metal junction in the electronic part of the electrochemical circuit, which is at the temperature of the cell, would not be able to exactly counteract the above situation. This problem is discussed in connection with Peltier effect in section VII,D,3.

In closing this section it is appropriate to reproduce a statement from Trasatti's work which enlightens the need for investigating the electron-transfer step --

> "....the behavior of electrons can bridge the fields of electrochemistry, physics and chemistry, and focusing the attention upon the electronic structure may reveal the underlying unity of many apparently diverse subjects."

O. INVESTIGATIONS ON TEMPERATURE EFFECTS

1. Introduction

There are few instances in the electrochemical literature where the role played by temperature has been considered. These have been sporadic and the intents on the investigations are various in scope. What follows is a grouping of representative works on the different aspects of the effects of temperature on electrochemical systems. This has been done in order to distinguish between investigations which are relevant, but of marginal concern, and those which are of importance for this research in providing additional information for reinforcing the foundation of the electrodynamic model.

2. Definition of Temperature

This concept has always been difficult to define clearly without arbitrary references, and in a way which can be directly measured. Temperature and energy are related to one another by the entropy concept and the form of the relationship is different for different substances. The concept of negative absolute temperature is generally regarded, at best, as an "amusing notion"; only Marvan[115] and Landau and Lifsic[116b] offer constructive discussions.

The Georgian temperature scale is regarded as the most appropriate to fit into the developing concepts of the electrodynamic model. Presented by Brostow[116], this scale is based on the definition of the value for the gas constant: $R_g = 1. \times 10^3$ (dimensionless) (where subscript g stands for Georgian) instead of the classical gas constant: $R_o = 8.31434 \times 10^3$ J kmole^{-1}°K^{-1}, in which substituting for R_g we obtain the conversion factor for the Kelvin scale: 1. °K = 8.31434×10^3 J kmole^{-1}. The equation of state of the perfect gas becomes: PV = T, and the Boltzmann constant: $\kappa = N_A^{-1}$, where N_A^{-1} is the Avogadro number. In this way we have the temperature expressed in terms of energy density, to represent only a part of the total energy stored in the volume element. The most convenient feature of this reasoning is that, at 10. K for instance, upon removal of one electron from the volume element, we still have a positive value of energy density, while instead we would have a negative value for the Kelvin scale.

3. Different Levels of Macroscopic Uniform Temperature

Most of the electrochemical work involving temperature is of this type in connection with reaction rates at various temperatures.

The series of investigations of Vagramyan's[117,138] group on metal deposition and dissolution from aqueous solutions can be seen as particularly interesting because of the high (for aqueous standards) upper temperature limit, 275°C, and for the ingenious technique used for observing the electrodes in the pressure vessel (optical fibres). The experimental results are in general interesting too. With increasing temperature it is found that:

- the exchange current density increases;
- the rate of anodic process increases at a greater rate than the cathodic process;
- both anodic and cathodic charge transfer coefficients increase;
- the standard exchange current for cathodic and anodic processes are practically equal above 275°C;
- the morphology of the deposit at high current density, goes from finely divided at 25°C to coarse crystalline at 250°C;
- the atomic hydrogen in the deposit is found at 25°C, none at 250°C;
- the preferred crystalline orientation changes.

Vagranyan's explanation of these results, for the nickel system, includes the following consideration --

> "Higher values of cathodic exchange current indicate that when the cathodic process takes place, as a result of continuous deposition of the metal, the electrode surface is more active than during dissolution."

The effect of temperature on the structure of copper has been studied by several authors. Barnes et al.[118] indicates that the usual sequence for the transition, with increasing current density, between ridge, platelets, blocks, and polycrystalline, is shifted at higher current density values for increasing temperature between 20 and 45°C. These statements are in agreement with the basic concepts of the electrodynamic model, as it will be seen in section VII,D,5.

4. Externally Applied Temperature Difference at the Liquid Junction Within the Electrolyte Maintaining Both Electrode/Electrolyte Interphases at the Same Temperature

This type of non-isothermal galvanic cell has been called electrolytic thermocouple; Haase has recently reviewed[119] his own work and that of the very few earlier investigations.

The fundamental work in this field appears to be Duane's[12 doctoral thesis produced under the guidance of Nernst, Planck, Warburg and others. I was fortunate to find a copy of this excellent work which gives quantitative values for the emf contribution to the total cell voltage due to liquid junctions kept at different temperatures -- the order of magnitude is 0.5 mV $°K^{-1}$.

Although the above considerations are beyond the limits of this investigation, they are nevertheless enlightening on the dependence of the cell potential on local temperature non-uniformity.

5. Externally Applied Temperature Difference Across the Electrolyte Maintaining the Two Electrode/Electrolyte Interphases at Uniform Different Temperatures

The classical review work in this field is by Agar[121] who called this type of non-isothermal galvanic cells, thermogalvanic cells. He applied Eastman's general treatment (see section II,F) to this particular type of electrochemical cells. They differ from the usual thermoelectric devices in the fact that one of the conductors, in which the temperature gradient exists, is ionic, while the other is electronic. Similarly, the difference from the type described in the previous section, is in that both thermocouple legs were ionic.

It must be stressed, however, that the temperature gradients lie entirely along the electronic and ionic conductors, that is, the electrode/electrolyte interphase regions are at uniform, even though different, temperature. Since this type of approach starts from the assumption that no temperature gradient exists at the interphase, this work is not immediately useful for the investigation of this thesis. Agar's treatment is, however, a careful application of irreversible thermodynamics to electrolytes. In particular, his treatment of transported entropy and heat of transport is one of the clearest available stressing the thermodynamical significance of the transfer of heat from one reservoir to another at the same temperature. In this connection, Agar deals with Soret and Peltier effects. Comments on the latter will be given in section VII,D,3.

The most recent and accurate treatment of thermoelectric and Soret effect measurements in electrochemical cells, and their use for the determination of the heat of transfer of cations is offered by Wagner[122]. Unfortunately, his work was published after the time this survey was terminated, thus this comment is unduly limited.

6. Externally Applied Temperature Gradient Across the Interphases Electrode/Electrolyte

Koryushin[123], in introducing his work, notes the absence of systematic investigations (1971) of the principles governing the deposition of metals at a cathode when there is a temperature gradient in the electrolyte. He cites only one report by Baraboshkin, which incidentally, is in molten salts systems. Koryushin studied the effects of the direction and intensity (max. $\Delta T = 50.C°$) of the temperature gradient on the morphology of the deposit of metallic copper at the cathode. He observed that with the heat flux directed from the cathode into the electrolyte (i.e. the cathode surface was hotter than the solution) the production of a smooth deposit, free from bumps and with a clearly defined columnar character was obtained. Instead, with the opposite temperature gradient (i.e. the cathode surface was colder than the solution) dendrites consisting of separate spherical crystallites were produced. Koryushin did not offer any explanation for this phenomena. It will be shown in section VIII,A that the electrodynamic model provides a simple immediate explanation for the above.

Marchiano and Arvia[124] studied the effect of nonisothermal free convection on copper electrodeposition kinetics, when a thermal gradient is superimposed. In particular, they calculate the variation of flow rate parallel and next to a vertical electrode, as a function of the temperature difference between the electrode and the solution, each being maintained at its respective temperature. Their paper has some unclear points related to the comparison of their calculated values with experimental works of other authors. It appears that in the case of copper electrodeposition under a ± 15.°C temperature difference, the effect of the nonisothermal free convection on the rate of reaction is weak.

7. Naturally Occurring Temperature Non-Uniformity Between the Electrode/Electrolyte Interphase as a Whole and Rest of the System

There are very few systematic calorimetric investigations in electrochemistry. The work of Thouvenin[125] may be regarded as the most advanced in this area, even though he was working toward the experimental determination of what he called -- electrolytic Peltier effect. Since his results indicated that the amount of heat evolved during electrode processes is different from the Peltier heat, there is a close relationship between his work and the argument of this thesis. A few words of comment are therefore useful. Thouvenin blames the theoreticians, who until recently, have considered the electrode/electrolyte interphase as a surface and not as a volume, and who have postulated that the entropy production is inexistent in the double layer. The electrochemical double layer has an extremely small thickness, but finite, in which the electrode reaction takes place, and to which an internal production of entropy that cannot be neglected, is associated.

He starts by saying that -- by definition, in order to have the Peltier effect, the system must not be at equilibrium, thus the thermodynamics of an electrode reaction must necessarily be thermodynamics of irreversible phenomena. Thouvenin then develops the entropy balance (internal production and exchange) for the volume of an electrode/electrolyte region constituted of a phase I (the electronic conductor), the interphase (double layer), and a phase II (the ionic conductor). His definition of the structure of the interphase is very interesting. It includes the double layer (Helmholtz and Gouy) possibly sandwiched between two diffusion layers, one on each phase side. The entropy production at the interphase is related to the electrochemical quantities by the expression:

$$T\, dS_i^{I/II} = J\, \tilde{A}_s = \frac{\tilde{A}}{z_r}\frac{s}{F}\, I = \eta\, I = R_s\, I^2 \qquad \text{II,0,7}$$

where:

T - the uniform temperature

J - the reaction rate

A_s - the electrochemical affinity

I - the current

z_r - the valence of the constituent ion r,

F - the Faraday constant

η - the cell overvoltage

R_s - the resistance relative to the voltage

and the subscript s refers to steady-state process.

Thouvenin stresses, however, that we cannot dissociate the entropy exchange from the entropy production since the Peltier effect is meaningful only when the system is not in thermodynamic equilibrium. Moreover, while the entropy production essentially depends on different experimental conditions of measurement, the exchange of entropy corresponds to the fundamental aspect of the phenomenon; thus, it is specified only by the junction considered. From this he deduced a more precise definition of the Peltier effect -- the Peltier heat is the quantity of heat involved at an isothermal junction of two phases, traversed by an electric current, when the irreversibility of the phenomena is negligible.

Thouvenin defines the molar heat of electrolytic Peltier for the electrochemical system as the quantity of heat involved because of the reversible passage from inside phase I to inside phase II, of one mole of electroactive ion r:

$$\Pi^{I/II} = z_r \ F \ \pi^{I/II}$$

where, $\pi^{I/II}$ is the Peltier coefficient relative to the passage of one unit of electrical current.

From this point on, as it can be seen from these last statements, Thouvenin[125] very unfortunately, goes back to consider the interphase as bidimensional, neglects the electron transfer reaction treating electrodes as liquid junctions, and considers reversible processes only. In fact, he does not use the entropy balance previously derived, in order to maintain the validity of the Thomson expression relating the Peltier coefficient to the thermoelectric power. Consequently, after having stated that for purely metallic couples there is no difference between the initial and the steady state Peltier heat, because at any instant there are no fluxes other than heat flux and electron flux (the electroactive charged species), he derives the steady state electrolytic Peltier molar heat as a function only of the difference between the transported molar entropies ($\bar{\bar{S}}_r$) of phase I and phase II:

$$(\Pi_r^{I/II})_s = T\ (\bar{\bar{S}}_r^{I} - \bar{\bar{S}}_r^{II})$$

Since the global energetic balance, corresponding to the passage of a current through an electrochemical junction indicated to him that during the experimental measurements, the different thermal phenomena superimpose to the Peltier heat, he evaluated these phenomena to determine under which experimental conditions he could eliminate their influence. Regarding the Joule heat, Thouvenin says that since this effect is proportional to the square of the current, while the Peltier effect is only directly proportional to the current, Joule heat can be eliminated either by using vanishingly small currents, or with a differential technique of measurement between two oppositely working identical electrode/electrolyte systems. To eliminate the Soret effect --

which is the diffusion of matter under the action of a temperature gradient -- it is enough to keep the system perfectly isothermal. The parasitic effect of purely metallic Peltier heats at the metallic junctions of the cell leads, is usually about one hundred times smaller than the effect being studied and is therefore regarded as negligible.

Now we reach a most important point -- the evaluation of what Thouvenin calls "polarization heat". From the expression [II,0,7] he recalls that the release of irreversible heat is associated with the existence of an overpotential at the electrode. He disposes of this problem by saying that in the domain around the electrochemical equilibrium, where the overpotential is less than 0.5 mV, the current is proportional to the voltage, and since anodic and cathodic overvoltages are equal in absolute values, for the same current of electrolysis, he proposed that a differential technique would eliminate the polarization effect. It would appear that Thouvenin has quite forgotten about the effect of the type of electrode reaction on the entropy balance, since at the anode we may have a positive ΔS with the corresponding heat being absorbed from the surroundings.

With regard to the question as to whether in the absence of agitation of the electrolytic solution, the concentration polarization increases with time in such a way that the anodic and cathodic overtension would not be equal any more, he answers that -- with constant current during a non-differential (one electrode only) measurement, the "absolute" value of the thermal debit remains constant regardless of the direction of the current, consequently the Joule effect and concentration polarization are very negligible compared to the electrolytic Peltier effect.

The comments on Thouvenin's[125] work may now be summarized thus:

- he did not mention whether the negative thermal debit was occurring during anodic processes and the positive with cathodic, although it would have been very interesting;
- he completely disregarded the electrode reaction in the interphase responsible for the change in type of conduction;
- he did not realize that, in the system studied, there are two types of Peltier effects -- one between ionic conductors (phase II and interphase) and one between electronic conductors (interphase and phase I).

In the light of the above comments I found it difficult to interpret his results obtained from zinc and cadmium amalgam electrodes in contact with aqueous solutions in the presence of supporting electrolytes, with oxygen free controlled atmosphere. The very small quantity of heat involved (microwatts) under the conditions indicated above, necessitated the use of a Calvet differential calorimeter by Thouvenin. Incidentally, he did not account for the heat of mixing of Zn or Cd in mercury at the cathode, probably because in his differential measurements the demixing value for the anode will cancel exactly out. Even with the shortcoming indicated, Thouvenin's work is a commendable one, and serves to illustrate the complexity of a thermodynamic analysis of electrode processes when the roles of the temperature and heat fluxes is accounted for. In fact, Thouvenin concludes by saying that (my literal translation) --

> "We can conclude that the heat of the electrochemical reaction (quantity purely thermodynamic) constitute the principal part of the electrolytic Peltier heat, the other contribution, of kinetic origin, being negligible."

A work most relevant to this research and at the same time the most unclear of the reviewed ones, is the letter to the editor of Elektrokhimiya by Gokhshtein[126] under the title - "Measurement of the Heat of Irreversible Electrode Processes" in the English translation. He seems to have correlated the amplitude of mechanical oscillations generated on a thin electrode with the heat evolved during the process when a periodic current with frequency of 10^3 -10^4 Hz is used. The superimposition of a direct current on the oscillating current permits the construction of heat-time curves, for irreversible processes. Under cathodic mode, the heat evolved W_c is larger than W_o (the heat evolved when no direct current is applied), while under anodic condition W_a is less than W_o, with deviations from W_o reaching 20% of its value, at the end of a transition period. The cathodic curve, after this transition period, increases abruptly to twice the value of W_o for which Gokhshtein offers the following explanation --

> "...is the heat at which water discharges and releases hydrogen (an irreversible process)."

In summary, the most interesting point is that, as time increases the cathodic curve rises and the anodic curve falls. This behavior, as it will be seen, appears to be in agreement with the experimental results of this thesis, and it is very unfortunate that Gokhshtein's experiment is not sufficiently described to permit quantitative interpretation - not even the method used to measure the mechanical vibrations which supposedly are related to the heat changes, is indicated! The only explanation that he gives for these results is:

> "As was shown by experiments [?] with different c [*the reagent concentration near the electrode, or the superficial adsorbate density*] and ω [*the frequency*], the difference among W_c, W_a, and W_o results from the fact that the exchange current is small and the overvoltages $\Delta\eta$ and $\Delta\eta_0$ corresponding to the currents Δj and j_o [*the direct current*] are large under the conditions in question. This is responsible for the appearance of a substantial alternating superficial-voltage component in the overall signal (because of $\Delta\eta$), its variation when the current j_o is applied, and the change in its sign (because of $[\Delta]\eta_0$). Solvent discharge occurs earlier at the same j_o when the exchange current decreases."

Gokhshtein's paper ends here, and his previous works which he cites, are of very little help. Also, the translation from the Russian original text, does not contribute to the understanding of this work.

8. Naturally Occurring Temperature Non-Uniformity at Interphase Measured from the Electrode Side

No work of this type on metal deposition and dissolution systems was found during the survey of the literature. However, a very interesting research by the Materials Engineers, Yahalom and Zahavi[127] on surface oxides electrolytic formation and breakdown must be mentioned in view of the agreement of their findings with the electrodynamic model. Even though as indicated earlier, studies of electrode/ electrolyte systems which form semiconducting layers in the interphase are beyond the scope of this work. These authors in their series of papers used the specimen bulk resistance variation during anodization to monitor the temperature variation of the electrode as a whole, they found that the crystallization of tantalum, aluminum, titanium oxides produced at the electrode surface, took place at everage temperatures far below those required in a furnace. They show that Joule heating does not suffice for crystallization of the whole oxide film, not even for titanium that has the lowest oxide crystallization temperature of the mentioned ones. They conclude that the breakdown of the oxides is controlled by the oxide/solution interface conditions rather than by the bulk of the oxide film or its history. These observations are very relevant to this thesis. It appears, however, that the temperature-measuring system used by

Yahalom and Zahavi did not permit the measurement of the actual surface temperature (the temperature of the oxide film), since the thermal effect on the resistance was generated by the temperature of the bulk of the specimen. In the experimental sections of this thesis, this problem of the bulk dilution of the surface temperature signal will be discussed.

P. TITANIUM DEPOSITION MECHANISM IN FUSED SALTS

The mechanism of Titanium electrodeposition (proposed in the author's M.S. Thesis[86], indicated the existence of an unaccounted amount of energy, released by titanium species during electrocrystallization. The mechanism is graphically presented in Fig. II,8 where:

E^* = Activation energy level

E_{III} = Ground state energy level of the anode surface

E_{II} = Ground state energy level of the ions in the electrolyte at large distance from the electrodes

E_I = Ground state energy level of the cathode surface, electrons in the Fermi level of the metal

E_0 = Ground state energy level of the transient entity

ψ^+ = Galvani potential at the anode interphase, plus the overpotential, as a function of the distance from the electrode

ψ^- = Galvani potential at the cathode interphase, plus the overpotential, as a function of the distance from the electrode

R = Reversible potential curve as a function of the distance from the electrode

Act. = Activation energy curve as a function of the distance from the electrode surface

Dis. = Dissolution energy curve as a function of the distance from the anode surface

The phenomenon of excess energy was explained as follows --

> "...the ion is activated up to an energy level at which an electron can escape from the solid state electron valence cloud on the cathode metal surface and be attracted to orbit at the valence

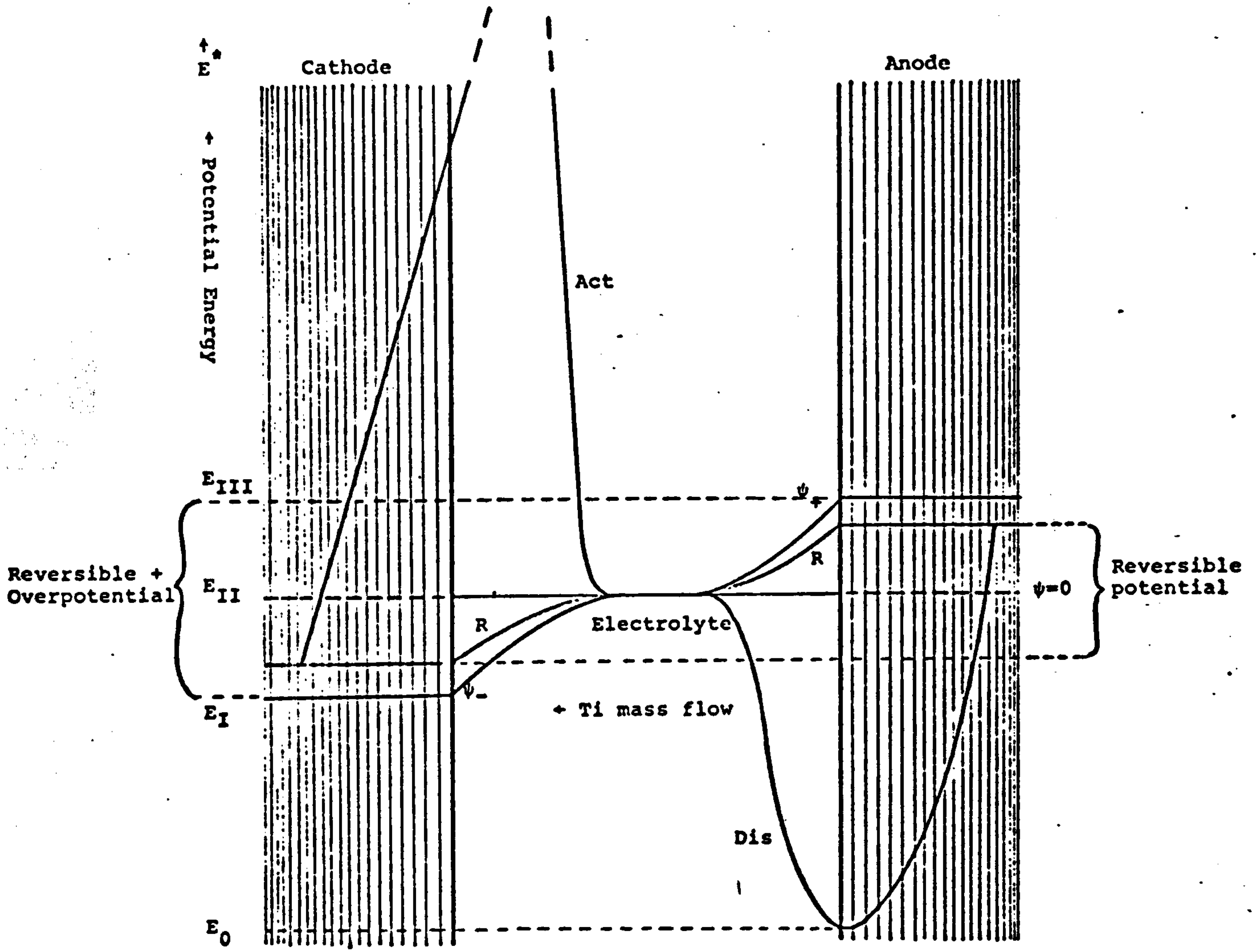

Fig. 3. - Curve of the change in energy for titanium electrolytic refining.

Fig. II,8 - Reproduced from the author's M.S. Thesis[86].

> level around the ion forming a neutral atom. At this moment the newly formed atom is still at the activation energy level. However, when the atom reaches the electrode surface it is at the lowest energy level of the cathodic system. Thus, an amount of energy equal to the difference between the activation energy and the electrode surface energy levels must be dissipated during the atom's advance from its original to its final position on the surface and then through the surface of the electrode. With electrodes having a low thermal conductivity, the dissipation of this excess energy will be slow, resulting in a build up of surface energy..."

The cooling effect (negative excess energy) was explained as follows:

> "...when one electron is removed from the titanium atom on the surface of the anode, but the remaining electrons have not yet had time to rearrange themselves in orbits closer to the nucleus, the entity is no longer an atom, but is not yet an ion in its equilibrium electronic state. This transient entity has an energy density lower than both atom and ion, that is, a smaller number of charges per unit volume. The energy level of the above defined entity is the lowest of the system, E_o..."

This work, which was essentially experimental[86] has been primarily responsible for generating the interest in the study of energy changes in electrode processes.

Q. SOME INSUFFICIENTLY UNDERSTOOD ELECTRODE PHENOMENA

1. Introduction

In order to collectively indicate the various kinds of phenomena, occurring at the electrode/electrolyte interphase, which are still poorly understood to date, the following paragraph has been included. The reason for their inclusion is their primary importance in practical industrial operating conditions and the possibility of explaining them in terms of the electrodynamic model.

The effects of ionic impurities, organic compounds, nature of electrolyte, temperature, and current density, on the physical characteristics of electrodeposited metals are experimentally well known, and a large body of results is available in the literature. The interpretation of these results, however, is largely fragmentary, and generally, applicable only to a specific set of experimental conditions. The mechanisms responsible for the resulting variety of deposit morphologies, and for the generation of such phenomena as internal tensile and compressive stresses, gas overvoltages, galvanoluminescence are not as yet clearly established.

What follows ia a brief review of some of the existing theories related to the above phenomena.

2. Organic Additives

There are several types of addition agents serving the different purposes of brightening, lustering, and leveling. To date there is no general theory of brightening, although several exist -- these are reviewed in a fairly recent work by Kaikaris[128]. The only aspect on which there appears to be agreement is that, the primary mechanism for brightening is deceleration of crystallization, by the insulating action of organic molecules adsorbed on the crystal nuclei thereby hampering their growth. Also, the formation of a near-cathode layer of colloidal particles in which the metal ion is reduced either by cathode electrons or by hydrogen, which saturates this layer, is another suggested mechanism. It is seldom specified whether the hydrogen is atomic or molecular. Interactions between colloidal particles and cathode electrons reduce the overvoltage and increase the current in the cell, but saturation of the near-cathode layer with colloidal particles slows the penetration of metal ions, hence the cathodic overvoltage is increased and the current decreased. Frequent repetition of this process shows in a auto-oscillation of the cathodic potential and cell current.

The above statement is a summary of a very interesting mechanism suggested by Kaikaris[128] and which can be related to the beneficial practice of pulse electrolysis (see ref. [86]).

The effect of most additives on the crystalline roughness of deposits has been recently reviewed by Luk'yanova et al.[129]. They show that in most cases with increasing current density, the reverse of the usual sequence of deposit morphology (smooth, rough, dendrites) occurs. Further, it is generally found that additives tend to increase the defect concentration in the electrodeposits.

In this context, it appears that the ad-absorption theories are having difficulties in explaining phenomena such as, for example, the cathodic potential increase observed in acid electrolytes, while a decrease is observed in cyanide electrolytes, when the same brightener is added.

3. Gases Overvoltage

It is well known that certain metals, which are above hydrogen in the electromotive series for aqueous solutions, can be electrodeposited in preference to hydrogen. This phenomenon is attributed to hydrogen overvoltage, and has been the subject of numerous and conflicting interpretations[75-78] [86]. The only aspect which finds everybody in agreement is the fact that it is a dynamic phenomenon, which depends primarily upon the value of current density and on the chemical identity and surface preparation of the metal electrode. We must note that the result of electrochemical reaction is the production of atomic hydrogen and oxygen and the formation of a bubble of molecular gas is not electrochemical but depends on bubble nucleation phenomena. Martins[130] experiments with supersaturated solutions demonstrated that to nucleate a bubble an energy input is required which will locally vaporize the liquid thus generating a site for gaseous change of phase.

Regarding the anodic evolution of oxygen, Bockris and Srinivasan[20] examined fourteen most probably mechanisms of the oxygen-electrode reaction, and attributed to the impurity content the difference between the rest and the reversible potential for the four-electron oxygen-reduction reaction.

Kaikaris[128] reports that there are conditions for which the hydrogen pressure inside the near-cathode layer is higher than the total pressure of the system -- this generates hollow metallic microspheres. These considerations can be correlated with the electropermeation of hydrogen into metals, which has been recently treated by Bockris et al.[131], and with the hydrogen cracking of metals studied by Rodriguez[132].

Very recently, Bockris and Subramanyan[133] returned on the subject of the hydrogen embrittlement of metals. They introduce their work with the following enlightening statement --

> "It is well known that the embrittlement proceeds easily if hydrogen is introduced into the metal electrolytically, whereas if hydrogen is introduced chemically (thermally activated hydrogen), the same degree of embrittlement is not obtained until the initial temperature is several hundred degrees above that at which the embrittlement can be made to commence in the electrochemical situation."

It will be seen in section VI,E,4 as to how this statement is in agreement with the concepts centered in the electrodynamic model, especially in view of the very high calculated values for fugacities, > 10^6 atm, which corresponds to real H_2 pressures of the order of 10,000 atm.

In addition, this result compares favorably with those presented by Macdonald and Barlow, as reviewed in section

4. Internal Stresses

As reported by Gangulee[134], the presence of residual stresses in electroplated films has been known for almost a century[135].

Kushner has discussed[136] the most reasonable theories for the origin of the stresses. These can be summarized as follows:

1) Hydrogen theory: atomic hydrogen enters the lattice of the depositing metal, momentarily expanding it, then diffusing both into the metal and into the solution. As diffusion continues, contraction of the lattice occurs with the formation of tensile stresses. This theory, however, does not explain the formation of compressive stresses in deposits of zinc and cadmium, which have relatively low cathodic current efficiency (large hydrogen codeposition) and should be susceptible to the same process.

2) Excess Energy theory: in view of the relevance of this theory to the electrodynamic model, Kushner's description is reproduced integrally:

> "A metal ion in the solution must surmount an energy barrier to be transformed from hydrated ion to a metal atom (or ion) firmly attached to the lattice. This may be thought of as a metal deposition overvoltage. Once the metal ion is over the hurdle, however, it possesses considerable excess energy; a group of such ions will

> have a higher temperature than their surroundings. As the hot metal ions deposit on the surface (they will have an average temperature several hundred degrees centigrade higher than their surrounding), the thermal gradient developed is very steep, both into the liquid and into the solid substrate. The very thin layer of hotter atoms forms a thermally expanded lattice and, on cooling, contraction ensues and tensile stresses develop.
>
> Even though these high temperatures have not been measured, this theory has some merit, since a number of high-temperature stable metal and alloy phases can be produced by electrodeposition at room temperature. But, thermodynamically speaking, there should be an opposite or refrigeration effect at the anode, for which there is no evidence. Furthermore, it does not explain why compressive stresses are produced."

3) Parasitic Water theory: proposed by Kushner[136], considers the chemical reactions of the water molecules of hydration with the metal ions at the electrode surface to produce oxides and hydroxides, which in turn are partially reduced to metallic form, thereby resulting in a decrease in volume which produces tensile stresses. Compressive stresses result when the oxide cannot be reduced as for zinc and cadmium. However, experimental evidence for this theory does not exist as yet.

4) Dislocation theory: a number of dislocations generated both by growth irregularities and by incorporation of organic molecules are assumed to generate the stresses. However, very recent calculations by Gangulee[134] show that an enormous number ($2x10^{11}$ lines cm^{-2}) of dislocations must

be present to account even for relatively small (10^8 N m^{-2}) stresses.

In addition, Kushner[136] makes this very interesting observation:

> "In very thin deposits, the stress will be minimized if the grain size of the substrate metal is made as large as possible." *and*, "The only exception to this is with deposits such as chromium which cannot bear the high tensile stress imposed and therefore crack."

Each of the above mentioned theories has important points, as we will see during development of the electrodynamic model.

Raub and Muller[64] have compiled most of the available data on stresses for aqueous electrodeposition of metals; their order of magnitude ranges from 10^8 to 10^9 N m^{-2}.

Very recently, Gangulee[134] made experimental comparisons between the mean planar tensile stresses in electroplated, from acid nitrate solutions, and vapor deposited copper films; these stresses were found to be of the same order of magnitude (6.1×10^8 N m^{-2}). Here, it is worth noting that these magnitudes are comparable to the stresses generated by phase change in solids[86]. Further, this author reports no evidence of stacking faults in both films. Gangulee explains the generation of the stresses in the vapor deposited film with the following words:

> "In vapor deposited film, the stress is principally caused by thermal mismatch between the substrate and the film, and subsequent dislocation movement."

The explanation for the stress in the electrodeposited film, however, cannot be considered satisfactory, because it associates the twinning faults with inclosures of additive molecules in the deposit, and it is well known that the stresses are generated also in the absence of additives.

Regarding the effects of current density and temperature on the magnitude of the stress, Lamb and Valentine[137] reported that in copper deposits from copper sulphate-sulphuric acid solutions, the tensile internal stress increased with current density and decreased with increasing electrolyte temperatures.

Vagramyan et al.[138] found that internal stresses for nickel electrodeposits decrease with increasing temperature; above 200°C there are practically no internal stresses.

For the effect of metal ion concentration in the electrolyte, Walker and Ward[139] recently reported that the internal tensile stress decreases as the concentration of copper sulphate in the bath is increased. The same was observed for cyanide baths. For zinc the compressive stress decreases with increasing zinc sulphate concentration, while for cobalt an increase followed by a decrease is reported. Incidentally, the role of hydrogen codeposition (as discussed in section VII,D,5) must be considered, because the hydrogen evolution is larger the lower the metal ion concentration. The very interesting phenomenon of stress "after effect" --

a decrease in the stress value, lasting two to three minutes after the current is switched off -- has been reviewed by Walker and Ward[139].

The effect of alternating current on the internal stress was studied, for the cobalt system, by Popereka and Avramenko[140] who found that the superimposition of a sinusoidal current of 200. Hz and ±57. mA cm^{-2} on a direct current causes the tensile stress value to go to a maximum at about 30. mA cm^{-2} of direct current. Above this value the stress then decreases with increasing direct current, and changes sign, becoming compressive at about 100. mA cm^{-2} of direct current. Thus, they seem to have established conditions for zero resulting stress.

The internal stresses of ferro-alloy depositions has recently been studied by Rotinyan et al[141]. They found that, in the iron-nickel system, the internal stress underwent two sign changes as the current density increased. Moreover, the magnetostrictive properties of this alloy depend strongly on its internal stress.

5. Deposit Morphology

The crystal orientation of electrodeposited copper as a function of current density and thickness of the deposit, has been recently reviewed by Bebczuk de Cusminsky[142,143]. He indicates that for deposition on single crystals of copper, the (111) plane appears to allow, when compared with (110) and (100), the largest thickness and the highest current density for epitaxial growth, just before the transition to polycrystalline deposition. Here it is important to notice that the (111) plane has the highest atomic density of all planes mentioned, and it will be seen how this result can be explained by the electrodynamic model.

Regarding the influence of the nature of the substrate on the structure of the deposit, it appears that some disagreement exists among the various authors. According to Pangarov, as reported by Dhananjayan et al.[144], the deposited fcc metals show a preferred orientation of (111) plane at low overpotential and of (110) at high overpotential. However, Brownsword and Farr[145] report that the crystalline structure of nickel which is fcc is not affected by the nature of the substrate, and the case of copper has been indicated in the previous paragraph. Further, very recently, Ivanova et al.[146] reported that the texture of the cathode materials has no influence on the orientation of chromium crystallites; for deposition on single-crystal support of (100) and (111) copper, the texture of chromium remained the same. However, Schlechten et al.[86] reported that titanium can be electrodeposited on titanium substrate in the form of a flat deposit, only up to a maximum thickness of 1.5 μm, whereas the smooth deposit may reach 125 μm on base metal substrates.

Again, we will see how the above phenomena can be explained in terms of the electrodynamic model.

The latest work on the influence of current density and temperature on the morphology and preferred orientation of electrodeposited copper is presented by Rashkov et al.[147] in which they suggest a new tridimensional mechanism associated with repeated twinning processes.

However, the basic question of why, in general, at low current densities we obtain smooth deposits and at high current densities, dendrites, still remains somewhat unanswered even though the effect of current density on deposit morphology is probably the best experimentally known.

The latest review of the factors affecting the morphology of electrodeposits is offered by Despic and Popov[148] who extended the theory of Barton and Bockris on the growth of dendrites. However, these authors still avoid the problem of explaining how the nucleation of a dendrite, from a flat surface occurs. In fact, after stating that any solid metal surface possesses a certain roughness, they say:

> "The induction period can be interpreted as the period needed for the exponential [*nature of the amplification of surface irregularities*], i.e., the avalanche-like, nature of the amplification suddenly to make the protrusion pierce the hydrodynamic layer boundary and become visible."

Despic and Popov, however, consent that the experiments gave only "fair" support to their theory. In fact, from the data reproduced on their Fig. 23 ([148] p. 233), one can just as easily interpret that there is no dependence of the dendrite initiation time on the solution concentration. This latter interpretation is in agreement with what the electrodynamic model predicts.

Further, it seems more meaningful to consider the dependence of the initiation time on the current density, instead of on the overvoltage as these authors did. Despic and Popov [148] offer an interesting review of the phenomenon of whisker growth:

> "...whiskers differ from dendrites because of the still larger ratio between longitudinal and lateral dimensions, and exhibit no tendency for side branching;
> ...while growing exclusively in one direction only, whiskers dissolve anodically at practically uniform rates at all sides and at an overpotential much smaller than needed for growth;
> ...a higher potential is needed temporarily for the initiation of growth (or continuation after interruption) than for growth at steady state;
> ...if the growth is interrupted for a longer period of time, then it may continue at the tip, but usually assuming a new direction, or else it may be completely prevented and a new whisker started elsewhere;
> ...if a constant rate of growth is maintained, by a constant current flow through the cell to the individual whisker tip, fluctuations of overvoltage are observed;
> ...whiskers have an increased electrical resistivity (2-3 times the bulk crystal) and increased tensile strength (10 times the bulk crystals).

Despic and Popov[148] offer also a description of the theories of Price and of Krichmar on whisker growth, which are based on the assumption of selective crystal plane adsorption of additive molecules; and they conclude that neither theory offers good reasons for the appearance of whiskers. Further, titanium whiskers have been grown[86] from fused salts under periodically reversed square wave current, without dead time between deposition and dissolution in the absence of additives.

Ibl et al.[149] in a very recent experimental work, in which they compare the effect of levelling agents as opposed to the effect of electropolishing, on the roughness of copper deposited at limiting current density, show that electropolishing uncovers crystallographic defects such as grain boundaries, dislocations, etc., thus fostering the initiation of a small roughness which is strongly amplified during deposition under limiting current density conditions. These authors, however did not attempt a mechanism explaining how levelling agents eliminate powder formation and give smooth deposits. Ibl[150], a decade ago, reviewed a large body of experimental results on electrolytic metal powder formation, and applied the concepts of mass transfer theories in order to interpret the results. Very recently, Despic and Poplov [148] improved on the treatment of the role of transport control in powder formation, but were forced to conclude that a model of the mechanism of powder formation is apparently not yet available. Also, one can present anomalous phenomena such as the tendency of zinc and cadmium to give powder at current densities lower than those needed for obtaining compact deposits which add to the difficulties of establishing a mechanism.

One of the very few statistical studies on the type of distribution of electrodeposited metal on an ideally smooth cathode surface, and of the influence of plating conditions on the type of distribution, has been made by Kovarskii and Golubev[151]. These authors accounted for a number of stochastic factors influencing the initial phase of the deposition. This seems to be the correct approach to be taken if real progress is to be made in this field.

6. Galvanoluminescence

This topic lies beyond the limits of the present investigation and it will be marginally considered only in connection with the work function (electron extraction energy). Some of the literature available is listed in references[152] as additional evidence of the existence of and of the necessity of accounting for the deactivation part of the electrode reaction path. This last statement is made in the light of the comment of Reynolds and Lumry[55] which was presented previously and is reiterated here:

> "Since over-all free energy changes in most chemical reactions are small relative to the promotion energies to excited states, in reactions with a large negative over-all free energy change the products may be formed in excited electronic states; it is to be expected that these processes will be found to emit radiation in the de-excitation of the products."

CHAPTER III. SPECIFIC CRITICISMS TO THE CURRENT METHODS OF ELECTRODE KINETICS

1. Introduction

The author of this thesis is aware that someone can suggest that he consider David Grayson's statement:

> "When I feel like finding faults I always begin with myself and then I never get any further."

Instead, these criticisms are intended to be viewed through the optics described in the introductory section of the literature survey, and they will be used to better the treatment of the electrodynamic model.

The current methods of electrochemical kinetics are largely based on the acceptance of Tafel-like expressions:

$$\eta = a + b \ln i \qquad \text{III,1}$$

where:

η - the overvoltage with reference to the reversible equilibrium potential

a - the intercept of the Tafel line to the overvoltage coordinate at a current density of 1. A cm^{-2}, and is assumed as equal to:

$$[RT/(\alpha zF)] \ln i_o$$

α - the charge transfer coefficient (or symmetry factor)*

i_o - the equilibrium exchange current density

z - the ion charge with its sign

R,T,F - the gas constant, absolute temperature, and Faraday constants respectively

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* their relationship will be discussed in the coming sections.

b - the Tafel line slope, and is equal to: $RT/(\alpha zF)$

i - the current density

The above expression can also be written as:

$$i = i_o \exp[\eta\alpha zF/(RT)] \qquad \text{III,2}$$

The type of empirical relation which enjoys the widest use is the combination of two Tafel expressions, one with parameters referring to the anodic portion of the current-overvoltage curve, and the other referring to the cathodic one, labelled respectively with the subscripts a and c:

$$i = i_o\{\exp[\alpha_a zF\eta_a/(RT)] - \exp[-\alpha_c zF\eta_c/(RT)]\} \qquad \text{III,3}$$

The above type of expression is variously presented as due to Butler, Volmer, Erdey-Gruz, Vetter, Delahay, Frumkin, Glasstone, Laidler, and Eyring. All these authors are careful to show the analogous treatment in terms of Eyring's chemical kinetics, the most explicit of which has been given, along with comments on Matthews work, in section II,J.

This type of approach is regarded as incorrect and overall responsible for the present state of electrochemical kinetics. A statement found in a most recent work by Bockris et al.[156] can be regarded as representative and is reproduced below --

> "The objection raised against the use of Boltzmann statistics in the Gurney-based model may be theoretically correct, but the same approximation has been used consistently in chemical kinetics with extremely good results. There does not seem to be any reason why it cannot be applied to electrochemical kinetics."

This thesis has been conceived with the aim of attacking the attitude expressed in the above statement, that is to make a complete differentiation between chemical dynamic and electrochemical dynamic methods.

2. Charge Transfer Coefficient

The charge transfer coefficient is the single most important quantity in electrochemical kinetics -- it is a measure of the efficiency of the conversion of electrical energy into chemical energy. Matthews and Bockris[74b] give the relationship between the transfer coefficient and the symmetry factor:

$$\alpha = s/\nu + \beta r$$

where:

α - charge transfer coefficient

β - symmetry factor

s - number of electrons transferred per act of the overall reaction

ν - stoichiometric number

r - number of electrons transferred in one act of the rate determining step

While an expression for its dependence on the overpotential has been recently proposed by Bonnaterre and Cauquis[38], a formulation for its dependence on temperature has not been attempted as yet. However, we have seen from the review of Vagramyan's work[117] that both cathodic and anodic charge coefficients increase with temperature, with the latter having a larger rate of increase. Nevertheless, in expressions of the type given by equation (III,3) the temperature dependence of the α is disregarded. Further, in the expression (III,3) $\alpha_a + \alpha_c = 1$ is implied, which is verified in various instances but not in many others. No explicit treatment could be found which explains the cases where $\alpha_a + \alpha_c \neq 1$.

3. Equilibrium Exchange Current Density

The phenomenon of the exchange current, this is still somewhat a mysterious concept, where it is unclear as to what is the correct mechanism -- is it analogous to a resonance, to an alternating tunneling, or is it an ion-atom alternating electronation and de-electronation? From the descriptions reviewed in section II,I all the possibilities seem to be acceptable, however, the energy required to sustain this phenomenon is vastly different for each mechanism.

In the development of the electrodynamic model the ion-atom electronation and de-electronation reaction will be considered as the mechanism which generates the exchange current. It is felt that this mechanism can best explain many of the observations relating to the exchange current (finite magnitude and dependence on chemical identity of the metal and the solution). These will be discussed in detail during the development of the model.

In order to gain some understanding of the order of magnitude of this energy, consider, as indicated by Bockris and Reddy, that for example, the value of the exchange current for hydrogen evolution reaction in 1. m H_2SO_4 on noble metals is in the milliampere per square centimeter region, then according to these authors, this corresponds to about 10 million monolayers of adsorbed hydrogen renewed per second, when the electrode is at the equilibrium potential. If one assumes a plane density of hydrogen of the same order as that for water (approximately 10^{16} molecules per square centimeter)*, the astonishing result of 1 mole of hydrogen atoms per second per square centimeter, is obtained!

This observation seems to indicate that an intense action exists in the interphase region, even though the hydrogen evolution reaction has an exchange current value which is not among the highest. It seems, therefore, not

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* The expression usually given to calculate this number, $\eta(H_3O^+)$ in the case of hydrated protons [2] for example is:

$$(H_3O^+) = 2rN\, c_{H_3O^+}$$

where:

r - radius of the water molecule (1.38×10^{-10}m)

N - Avogadro's number (6.0221×10^{26}kgmole^{-1})

$c_{H_3O^+}$ - concentration in kgmole m^{-3}

and for one mole gives: 1.66×10^{13} H_3O^+ cm^{-2}. This result is not correct because it is obtained by using the bulk concentration value of protons, thereby regarding the electrolyte side of the electrode/electrolyte interphase as equivalent to any plane in the bulk of the solution.

realistic to assume this region as having only the two dimensions of a surface; instead a volume interphase, of small but finite thickness, should be considered.

Moreover, considering the probability of high energy states for the ionic species, in order to sustain an exchange current of the above magnitude we must consider a volume in which this number of excited species, per unit time, can be expected to be distributed; since it will not be physically possible to naturally have so many excited ions at all times in a plane one atomic layer thick.

Further, the metal atoms of the electrode surface, are all at about the Fermi level at all times. They cannot, therefore, provide the energy to excite the species for the reaction in the reverse direction, unless there is some by-product energy from the direct reaction, which is momentarily and locally stored in the surface atoms. This energy can then be partially transferred to excite the species for the reverse reaction.

At this point, it seems clear that the treatment of the exchange current applied to a tridimensional interphase must be different from the traditional treatment applied to a bi-dimensional interface; the existence of an excess energy is the necessary condition required for maintaining an exchange current.

Finally, it can be seen that the effect of ionic concentration is not considered if one examines expressions like (III,3) where the possible dependence of the exchange current on composition is omitted.

4. Temperature and Energy Density

It follows from the considerations made in the previous section that the temperature of the interphase, even at the equilibrium potential, is not equal to the system temperature, because of the exchange current that generates a small, but finite, excess energy. Thus, the most important criticism, and from which this research originates, is the consideration of the role of temperature. With the exception mentioned in the literature survey, it is generally neglected. The temperature is regarded as a constant at any time and at all points along the reaction coordinates at the electrode/electrolyte interphase. Even speculations on the possibility of having the interphase at a different temperature than in the bulk of the electrolyte are rare.

Analogous criticisms can be made regarding the lack of accounting for the energy density variation along the reaction coordinates.

5. Current Generation

The next important criticism is in regard to the concept of current flow through the electrode/electrolyte interface; that is, the generally accepted assumption that electrons and ions pass across the electrode/electrolyte interphase. This assumption probably derives from the fact that for the ion-transfer mechanism, the thermodynamic conditions for equilibrium require that the electrochemical potential of the potential-determining species be equal in both phases between which the ions are transferred.

However, there is not, and there cannot be a charge transfer -- a flow of current through the interphase -- but only a generation of current within the interphase. This is followed by an exchange of electrons between the metal electrode and the interphase, and an equivalent exchange of ions between the interphase and the electrolytic solution. Therefore, the previously stated assumption seems to indicate that the concepts of redox reaction (electron exchange between ionic and/or gaseous species at an inert electronic conductor) and the metal/ion reaction (ion-atom transition) have become interconfused.

Further, this might also be the explanation for the difficulty met by those workers seeking a value of the electrolytic Peltier effect as reported in section II,O,7 when they fail to realize that at the electrode/electrolyte interphase there may be two Peltier effects: one at the electrode/interphase which is electronic and the other at the interphase/electrolyte which is ionic. This follows from the definition of the Peltier effect which only exists for the same charge carrier in two phases having the same type of electrical conduction.

6. The Concept of Active Species

In the description of Eyring's rate theory, the term "activated" complex is generally used. I have always felt that this term is inappropriate because it seems to imply that the reagent species are passive bystanders, subject to some external forces, and not the active participants of the process.

I would rather use the term "active" complex, which, however, requires a complex quantum-mechanical treatment for the description of its energy. It was probably in order to avoid this difficulty, that Eyring's rate theory ignores the manner in which the "activated" complexes are formed.

7. Reaction Barrier

Most of the authors mentioned in the survey, consider the activation energy barrier as a sort of physical obstacle -- a "hill" -- over which the ions must climb to be reduced (apart from the tunneling probability). However, in two instances, Hush in section II,G,2 and Laidler and Tweedale in section II,H, the speed with which the ions cross the barrier has been considered. This is an important piece of information required in order to better understand the physical meaning of the activation of a reaction.

8. Energy and Potential Energy

As it was mentioned in the literature survey (see section II,G,2) many authors have used potential energy vs. reactants distance curves to describe the electrode processes along the reaction coordinates. However, potential energy is a concept of thermostatics. In thermodynamics we deal with potential energy changes which are the measures of the energies involved in the process. This was done following Butler's treatment for proton transfer reactions, in which (see section II,G,3) by superimposing two potential energy curves for the separate interactions of hydration between water molecule and proton, and of adsorption between the metal and the hydrogen atom (helped by water repulsion) he obtained a crossing point which can only be interpreted to mean that the electron transfer could take place at distances from the electrode smaller than that of the crossing point of the two curves. Instead, most researchers who have followed this approach considered the crossing point as the equilibrium value of a reversible reaction, disregarding, therefore, that the nature of the interacting species depends on time. That is, before the electron transfer occurs we have an interaction involving an ion, while, after the electron transfer has occurred, the interaction involves a neutral species. Thus, we have two different systems which cannot be in equilibrium because they belong to different time periods. This interpretation is in agreement with one of the most important assumptions of Eyring's rate theory, which states that the "activated" species travels, in the transition state, in one direction only and it is unable to turn back -- this is the essence of Eyring's special type of dynamic equilibrium.

In summary, by working with potential energy curves, one disregards the dynamic nature of the electrode process. Instead, energy curves should be used for the purpose of determining the location and the energy of the active species.

9. Electrons and the Potential

As it has been reviewed in section II,M,4, electrons are properly defined as full fledged negative charge carriers, in electronic as well as ionic conductors. However, in the electronic conduction section of the electrochemical circuit, they are the only charge carriers. It is probably for this reason that the electron traveling the electronic part of the electrochamical circuit are generally regarded as entities external to the electrochemical system. This fact may give some insight into the reason why the concept of potential does not seem to be easily understandable. In fact, this term -- potential -- is not strictly correct by itself and many authors[2-153] are precise in stressing that it should be referred to as potential difference. However, this definition is still not informative enough, since it does not answer the questions -- difference of what quantity, and between which species?

I believe it should be described as the difference in potential energy between two electrons in different points of the electrochemical circuit, inclusive of the electronic part. This is a prerequisite that permits what is felt to be a correct and complete energy balance of the electrochemical processes.

10. Non-Applicability of Phenomenological Relations for Calculating Electrode Entropy Changes

As reported in section II,D, Prigogine's and Sanfeld's[9] local formulation of thermodynamics states that in every macroscopic* region of a system the entropy production rate per unit volume, due to irreversible processes, is positive. Thus, they define the entropy density and the entropy flow, or exchange between neighboring regions. They then suggest that the entropy can be considered as directly relating thermostatics with thermodynamics since it depends on the same variables whether the system is or is not in an equilibrium state.

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*Instead of "macroscopic" region, I would rather use the term chemical molecular region, as opposed to microscopic for nuclear physics region since this may more clearly define the size of the system we are considering.

In order to evaluate the entropy production Sanfeld and Prigogine suggest that the Gibbs formulation for the change in entropy density:

$$\frac{d\bar{s}}{dt} = \frac{1}{T}\frac{d\bar{e}}{dt} + \frac{p}{T}\frac{d\bar{v}}{dt} - \sum_{\gamma}\frac{\bar{\mu}_\gamma}{T}\frac{dN_\gamma}{dt}$$

where:

$\bar{s}$ - entropy density (per unit mass) in a non-uniform system with a local mass velocity ω

$\bar{e}$ - internal energy density

$\bar{v}$ - specific volume

$\bar{\mu}_\gamma$ - mass electrochemical potential of component γ

N_γ - mass fraction

which can be regarded as a good approximation for slow chemical reactions where an equilibrium distribution around a common mass velocity exists.

This, in other words, is the general theory of near-equilibrium processes, commonly used[9-19-121] as the basis for deriving the expressions relating various electrochemical phenomena. However, the validity of this method is restricted to systems which --

(1) are in the neighborhood of reversible equilibrium; thus, no chemical reaction should occur, or if it does, the products must always be in equilibrium with reactants, and must not introduce new components in the phase rule sense;

(2) have linear reciprocity relations between the generalized forces and the rate of the process;

(3) follow the selection rule for the interference between irreversible processes of different tensorial character; or the possibility of thermodynamic matching of fluxes because they are influenced by common generalized forces;

(4) are in mechanical equilibrium; linear gradient of external forces.

The Knudsen cell, for example, may represent such a type of system. It can be described as being formed by two vessels containing perfect gas at different temperature, which communicate by means of a capillary (limiting small mass flow). In this system there are two irreversible processes with generalized forces pointing in the same direction -- transport of matter with flow rate proportional to the pressure difference, and the heat transport proportional to the temperature difference between the vessels.

Unfortunately, it seems that electrode processes at which chemical reactions occur at measurable rate, can not be considered as having the required characteristics mentioned above. In fact, an infinitesimal overpotential causes the mass to flow freely, and the relationship between them is not linear. Not even the potential drop through the electrode/electrolyte interphase can be considered as linear as will be discussed in section V,7. Furthermore, in section IV,5, in discussing the principles of symmetry for electrode reactions, we will see that the interphase region is not isotropic nor even centrosymmetrical.

All these complications are present even before consideration is given to the effects produced by the temperature and the energy density profiles existing at the interphase region which is the major thrust of this research.

11. The Mechanism of Charge Transfer

We can conclude this chapter of criticisms by realizing that the major reason for the existence of the difficulties and imperfections in the understanding of electrochemical phenomena mentioned in the previous pages, is the fact that the actual mechanism of the charge transfer process at an electrode is still not very clear. As we have seen during the course of the literature survey, several models have been proposed to explain such a process but none of them have been completely successful in describing the process.

CHAPTER IV. THE ELECTRODYNAMIC APPROACH TO THE STUDY OF ELECTRODE PROCESSES

1. Introduction

In the light of the observations and remarks previously presented, it is worthwhile stating what the electrodynamic approach to the study of electrode processes entails such that it will allow for an accurate description of the energy changes occurring at an electrode/electrolyte interphase.

It appears from the literature survey that most authors of electrochemical kinetic works can be separated into two groups, represented by two antithetic mechanisms assumed to describe the electrode reaction -- ion-centric and electron-centric, as Bockris and Reddy[2] would say.

The electrodynamic approach considers both types of mechanisms as occurring simultaneously to mutually help in performing the electrode reaction. Appropriate concepts, fundamental to this approach, can be found in many of the works mentioned in the literature, when these treatments are viewed in a manner which does not assume the values of energy density and temperature at the electrode/electrolyte interphase as constants, which is not unlike the generally accepted assumption that the composition of the interphase is not the same as that of the bulk of the electrolytic solution.

Historically and still today, the values of electrochemical variables such as metal ion concentration, current density, temperature, degree of agitation, etc., which are common in industrial practice, have always been empirically adjusted in order that phenomena like diffusion, ad-absorption, dissociation of molecules and complex ions, nucleation of deposits, etc., may be optimized so as to minimize the hindrance and/or to enhance the beneficial effects on the process yield. Doing this resulted in setting, under those conditions, the charge-transfer stage as the rate controlling step; in fact, in most electrode processes all other steps behave rather ideally, as judged from experimental observations.

Therefore, most of the answers to unclear electrochemical phenomena are to be found in the study of the charge-transfer step, which is also the most distinctive feature of electrode processes over chemical ones.

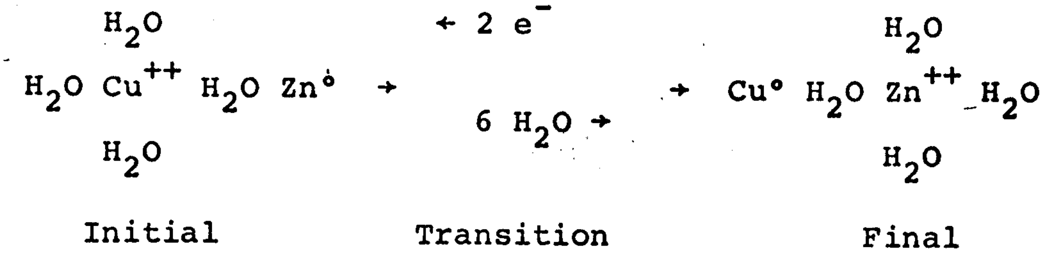
Positive indications of the correctness of the approach adopted in this thesis may be seen by studying published works in the new field of "Electrocatalysis"[156-72], which has been recently introduced, and appears to be an elegant way out of the impasse, Thermostatic Electrochemistry/ Chemical Dynamics, in the description of Electrochemical Kinetics. In fact, without abandoning their established theoretical treatments on equilibrium electrochemistry, several authors now feel free under the new label to speculate on far-from equilibrium electrochemical systems. This new attitude, however, must be brought back to our electrolytic bath to obtain real progresses in this area.

2. Difference Between Chemical and Electrochemical Reactions Regarding Their Energies Spatial Distribution

Consider, for example, the overall reaction:

$$CuSO_{4(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + ZnSO_{4(aq)}$$

The chemical mode of accomplishing this reaction (cementation process) can be, oversimplifying, pictured as follows:

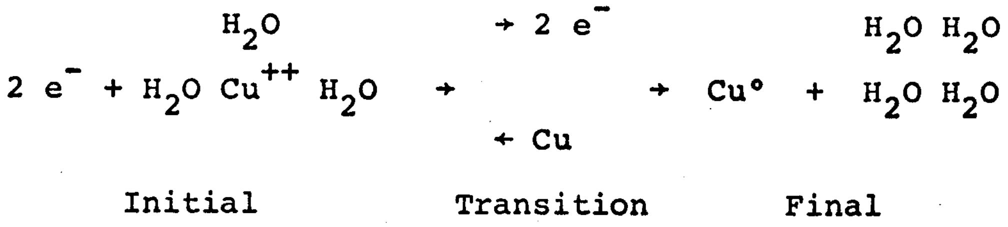


$$\begin{array}{ccc}
\begin{array}{c} H_2O \\ H_2O\ Cu^{++}\ H_2O\ Zn^{\circ} \\ H_2O \end{array} \rightarrow & \begin{array}{c} \leftarrow 2\ e^- \\ \\ 6\ H_2O \rightarrow \end{array} & \rightarrow \begin{array}{c} H_2O \\ Cu^{\circ}\ H_2O\ Zn^{++}\ H_2O \\ H_2O \end{array} \\
\text{Initial} & \text{Transition} & \text{Final}
\end{array}$$

The final state energy is of an order of magnitude comparable to the initial one, differing from it only by the magnitude of the free energy change of the general reaction. The electron-transfer act and the water-atom-ion exchange process occur in the same region in space.

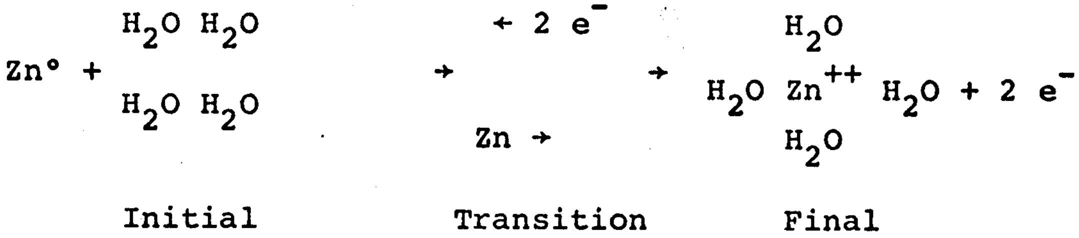
The electrochemical mode instead, is divided into two half reactions (Daniell cell) occurring at electrodes located in different regions in space, and an oversimplified picture can be drawn as follows:

(1) at the cathode



$$2\ e^- + \begin{array}{c} H_2O \\ H_2O\ Cu^{++}\ H_2O \end{array} \rightarrow \begin{array}{c} \rightarrow 2\ e^- \\ \\ \leftarrow Cu \end{array} \rightarrow Cu^\circ + \begin{array}{c} H_2O\ H_2O \\ H_2O\ H_2O \end{array}$$

(2) at the anode



$$Zn^\circ + \begin{array}{c} H_2O\ H_2O \\ H_2O\ H_2O \end{array} \rightarrow \begin{array}{c} \leftarrow 2\ e^- \\ \\ Zn \rightarrow \end{array} \rightarrow \begin{array}{c} H_2O \\ H_2O\ Zn^{++}\ H_2O \\ H_2O \end{array} + 2\ e^-$$

The half reaction occurring at the cathode has the initial state at a much higher potential energy value than the final state, thus a release of energy to the local surroundings must occur. On the other hand, the half reaction occurring at the anode has a final state which has a much higher potential energy than the initial state, thus energy must be absorbed from the local surroundings. The connection between the two halves of the overall reaction is provided by the electrons; the stability of which (relative magnitude of their potential energy) in one element or in the other, determines the direction and contributes to determine the net rate at which the reaction will proceed.

As stated by Reynolds and Lumry[55] (reviewed in section II,G,2), the "promotional" energies are much larger than the overall free energy changes in most chemical reactions.

Thus, the electrochemical mode of the reaction, spatially separating the two half reactions, succeeds in resolving the energy remaining from these promotional energies, individually for each product.

In the chemical mode for the general reaction, the above cathodic release of energy and anodic absorption of energy are mostly mutually compensating, since they occur in the same region in space.

In summary, we can see that in using the electrochemical mode, there are two more possibilities for external control of the thermodynamic behavior of the overall reaction than when the chemical mode is used. These are enumerated thus:

(1) We can alter the electron direction and rate of supply by interposing, for example, a power supply in the electronic part of the circuit;

(2) We can alter the energetic conditions of the two reagents and of the two products, independently, interposing, for example, a liquid junction or a temperature gradient in the ionic part of the circuit.

These observations are obvious, nonetheless their use and complete account are seldom considered. Therefore, we must attempt to make as complete an analysis as possible of these advantages of the electrochemical mode over the purely chemical mode of reactions.

3. Difference Between Chemical and Electrochemical Reactions Regarding Their Energy Efficiency

It has been reiterated that electrochemical systems are a special kind of energy converters; let us now make a comparison with purely chemical-dynamic processes.

In chemical dynamics the energy involved in the reaction is supplied or is obtained mostly in the form of sensible heat; the efficiency of the processes of matter conversion or generation of energy are restricted by Carnot limitation.

In electrochemical-dynamics we supply the system with energy for the reaction in the form of electrical energy, i.e., electrons potential energy difference, or we obtain energy from the system in the form of electrical energy.

Contrary to pyrometallurgical reactions in which we supply ΔH to the reactants, in electrochemical reactions we supply ΔG (by applying a potential difference $E = \frac{\Delta G}{nF}$) which is completely used entirely for the reaction. In analogy with the potential energy of a falling body $mg(h_2-h_1)$, the energy of electrons falling through a potential difference, $e^-(V_2-V_1)$, is completely used up. The difference in energy between reactants and products, instead of being expressed as a difference in increase or decrease of translational motion of molecules and associated entropy changes, the free energy change for the reaction, is expressed as a difference of electron "pressure".

Therefore, the major difference is that in electrochemical reactions there is a charge transfer whereas for a chemical reaction there is a heat transfer.

The above observation that electrode processes are able to operate much closer to 100% energy efficiency than purely chemical processes, seems to be another clear indication that electrochemical dynamic processes have very different features when compared with chemical dynamic processes. Moreover, this freedom from intrinsic limitations gives the electrochemists an additional breadth in comparison with the chemists, in that it is no longer necessary to consider hypothetical situations which cannot always be realized in practice (infinite dilute solution, reversible equilibrium, and the like). Consequently, throughout this study of electrochemical processes, only conditions which are common to industrial operations will be considered.

4. Energy and Potential Energy of Charged Species

As it was pointed out in sections II,G,3 and III,3 the concept of the difference between energy and potential energy is of fundamental importance.

We will begin by stating the general definition of potential energy usually found in the literature; this particular one is partially reproduced from Sonntag and VanWylen[166] --

> "For the anharmonic oscillator, the potential energy curve tends toward a limiting value as the distance of separation becomes very large, that is, as the molecule dissociates into two separate atoms. This value is commonly taken as the zero of energy, such that the energy at the minimum point of the curve is -D, which is called the total dissociation energy of the molecule. However, we realize that this minimum point is not accessible to the molecule, which in its ground state still possesses a zero-point energy corresponding to v=0 [*the vibrational quantum number*]. Thus, the observed dissociation energy of the molecule will be that corresponding to the ground state v=0, with an energy $-D_0$ relative to that of the dissociated molecule."

The potential energy function of an anharmonic oscillator as it is usually given, is reproduced in Fig. IV,1.

For the purpose of indicating the method to be used in attempting the numerical determination of the values of the energy and of the potential energy, let us consider the case of an oversimplified anharmonic vibrational interaction between two opposite charged species. The first observation we can make is that the terms energy and potential energy are used interchangeably, as one can see from the label of the ordinate in Fig.IV,1, and from its caption. However, since the curve represents the values of the potential energy contained within the system formed by the two interacting species, at the instant in time when they have particular separation distances, the species are thought of as being held in these positions, thus, the curve does not include the kinetic energy of the species relative to each other. Consequently, the curve in Fig.IV,1 does not give the value of

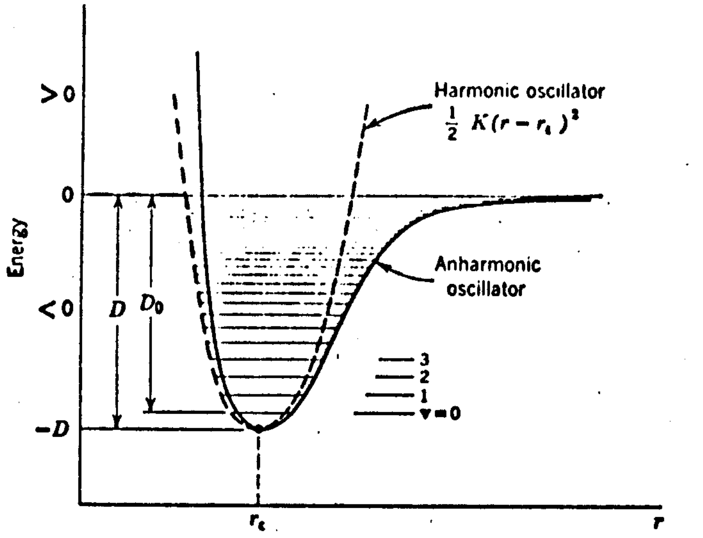


Figure 5.9 The potential energy function of an anharmonic oscillator.

Fig. IV,1 - Reproduced from Sonntag and Van Wylen[166].

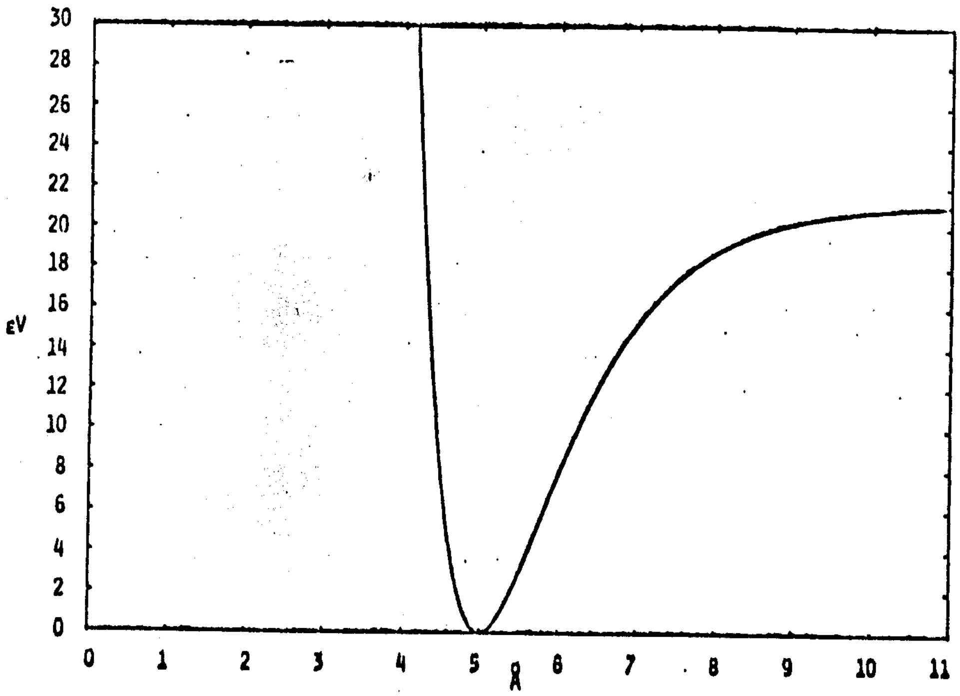


Fig. IV,2 - Curve representing the potential energy change as a function of separation distance.

the energy that the interacting species have as a function of distance, but only gives the potential energy the system has when the interacting species are at a given, fixed distance apart. From the above consideration it seems more appropriate to label the ordinate of Fig.IV,1 as potential energy.

The second observation regards the use of negative values for energies. This custom does not help in the understanding of the physical meaning of interactive processes. It is therefore, regarded as preferable to set as the zero value of potential energy for the system, the value corresponding to the equilibrium separation distance. This, incidentally, is consistent with the definition of equilibrium state of a system -- potential energy equal zero. Of course, the zero potential energy point will now correspond to $-D_o$ in Fig.IV,1, the observed dissociation energy.

The ideas expressed above are now depicted in Fig.IV,2 which presents the potential energy function which will be used in the study of the electrode processes.

At this stage it is now possible to obtain the numerical values of the energy which the species have at any instant during the time of their interaction, by using the potential energy curve and recalling that the change in the energy of the species is proportional to the difference in potential energy which has occurred in the system. Thus, the occurrence of the interactive process transforms the potential energy of the system into energy carried by the individual species forming the system. Conversely, external energy supplied to the species is transformed into an increase in the potential energy of the system.

To clarify this point, consider in Fig.IV,2 the case of the two opposite charged species at their equilibrium distance (5 Å): the species have their characteristic energy but the system has zero potential energy. If we now supply the species with, for example, 15 eV of additional energy, the system will store this energy in the form of potential energy, and the separation distance between the species will increase to about 7 Å; thus the potential energy of the system now is 15 eV. However, if we were to let the attractive interaction proceed, starting from the separation distance of 7 Å, the species will return to the equilibrium distance. In doing this the system will loose potential energy but the species will gain kinetic energy down to the point of equilibrium in which the 15 eV of energy which were supplied at the beginning are made available to the surroundings by the system. Actually, the energy available will be less than 15 eV if the interactive species are immersed in an environment in which neutral and/or polar species are present, because of the energy dissipated due to minor interactions.

This important point may be summarized by stating that in live dynamic interactive processes the decrease in potential energy of the system always results in an increase in energy of the species forming the system, unless the processes are conducted in such a way as to allow the species to come to the equilibrium distance at a limiting small velocity. This, incidentally, is in agreement with the definition of reversibility.

In conclusion, the determination of the energy which the species have at the end of an interactive process in which there is a potential energy decrease for the system, is a very important aspect of the study of electrode processes, since it will indicate the energetic conditions of the electrode reaction products and thus, the amount of the deactivation energy. Moreover, the rate at which the deactivation energy is released will determine the energy density (temperature) of the region where the products of the electrode reaction are formed. This approach is regarded as appropriate for the study of electrode reactions.

5. Principles of Symmetry

A brief consideration of the Neumann-Curie principle is useful in the development of the reasoning for the electrodynamic model. The application of it to electrodic systems has been investigated by Piontelli[19] and a summary of this concept is given below:

Elements of symmetry, common to the causes (active and passive) must be found in the resulting phenomenon (effect), which may also result in being richer of symmetry elements than the ensemble of the causes. Hence, from the absence of some elements of symmetry in the effects we can always infer the absence of the same elements in the ensemble of the causes. In particular, the elements of symmetry of a medium, in the presence of a generalized perturbation cannot be less than those which are common:

(a) to the medium in the absence of the perturbation

(b) to the perturbation itself

The effects of the perturbation are properties of the perturbed medium and they must have all its elements of symmetry. However, the absence of some of the elements of symmetry in the ensemble of the causes may not result in the absence of the same elements in the effects.

The necessary (but generally not sufficient) condition for a given physico-chemical phenomenon to occur, is that among the elements of symmetry characteristic of the ensemble of causes (active and passive) elements incompatible with the occurrence of the phenomena must be absent. In the simplest electrode process we can attribute to the gradient in electrochemical potential the character of generalized perturbation having as an effect the generation of current at the interphase region. This effect (generation of current) in turn produces other effects -- modification of the physico-chemical characteristics of the electrodic system as consequences of the occurrence of electrochemical reactions and their qualitative spatial distribution, and of the circulation of current and its quantitative spatial distribution. The generalized perturbation -- the electrochemical field -- has an isotropy axis normal to the electrode surface, and anisotropy may be present if the crystallographic orientation does not correspond to an equilibrium structure. But even in the absence of local imperfections, we must consider the existence of tangential components of the current density vector, due to the kinetic anisotropy (for example Zn deposition) -- the non-uniformity **of the gradient in electrochemical potential in various** points of the electrochemical system during a live process.

As elements of symmetry of the ensemble of causes we have only the planes and axis normal to the metallic surface. The interphase region, by the definition of its formation in kinetic equilibrium given earlier, is always anisotropic.

Thus, if the electrode surface has [illegible] of symmetry, the ensemble of causes has such axis, and we must find it in the effects.

The above considerations are useful in making up for the inadequacies of the phenomenological relations in the estimation of the production of entropy.

6. Interpretation of Entropy

Recalling the molecular interpretation which defines the entropy as the measure of the possible distribution of species in a system, we can show that -- $S = f(T,V,n)$ -- by using the customary example of the container divided into ten cells among which two particles can be arranged. By setting one particle in any cell and the other in the remaining we can calculate that 45 possible different distributions are available.

The effect of volume increase on the value of entropy can be seen by allowing the two particles to be distributed for example, in a volume twice the previous. Thus, among twenty cells the number of possible distributions rises to 190.

The effect of an increase in the number of particles in the system is shown by setting in communication two ten-cells-two-particles systems similar to the above indicated, to have a single system of four particles in twenty cells; by setting two particles we have (45x45) = 2025 possibilities.

This number of possible distributions is usually termed W, and its relationship with the value of entropy is given by -- $S = \kappa \ln W$ -- where κ is Boltzmann's constant.

The effect of an increase in temperature on the value of entropy, that is, the relationship between temperature and entropy change is a most complex one and cannot be demonstrated using the above analogue. In fact, the definition of these two quantities independently is a difficult task, their product is energy.

Now, in electrochemical processes, which are systems composed by opposite charged interacting species, the interpretation of entropy has an additional energetic physical meaning. In fact,any two opposite charged species, at any instant in time, can be thought of as forming an interacting system with energy stored in the form of potential energy, as discussed in section V,7.

The effect of a volume increase is to allow a larger amplitude for oscillation (more stretching) so that the system can absorb more energy by transforming it into potential energy stored in the system. Thus, we say that the system has its entropy increased, and if the energy cannot be absorbed from the surroundings the system temperature will decrease and so will the energy density (per unit volume).

The increase in the number of species correspondingly increases the number of potential energy interactive systems.

The entropy is thus increased and if the volume remained constant, then the energy density and the temperature are also increased, because of a more crowded environment in which the individual (two species interactive system) maximum potential energy value is decreased. Further, this addition of species to a volume is usually pictured as occurring quasi-statically, that is the species are considered as not being associated with kinetic energy. However, in most live dynamic electrode processes the species possess translational energy which they bring along into the volume. This results in additional gain in energy density in the receiving environment, therefore, also in an increase in its temperature.

Now, the effect of supplying energy in the form of heat to the system at a constant volume, will result in an increase in potential energy stored in the system. Thus, the energy density and temperature will increase, but not the entropy. In fact, a reduction of entropy can be predicted in agreement with Helmholtz free energy change with temperature.

At this point, Eastman's entropy theory (as reviewed in section II,F) must be introduced to fully account for all the changes in entropy and heat effects occurring at the electrode/electrolyte interphases.

The semiquantitative interpretation of the electrode processes will be conducted along the lines indicated above.

7. Concept of Interphase

At this point we have seen that, indeed, in electrode processes we have a non-uniform distribution of charges and matter at the interphase. More importantly, we have seen in point n.1 of the Synopsis and in the course of the literature survey[13] (section II,E), that it is difficult to numerically evaluate the difference in chemical potential between the same element in neutral form on the electrode (μ_{Me°) and in ionic form in solution (μ_{Me^+}). Since these two values are different under any condition, as we saw for example during the discussion on the exchange current (section II,I), the interphase must be there to allow for a gradient in the physico-chemical quantities of the element considered. No discontinuity (infinite gradient) can exist between phases within any time period; this is in analogy to the activity of metallic systems in which solid solutions must always exist to ensure finite activity gradients between phases. Thus, we do not have a direct exchange of matter between metal electrode and electrolytic solution, but a transfer between these and the interphase region. Therefore, the application of an external electric field tends to displace charged species and to localize the energy primarily in the interphase layers, thereby generating an energy density profile. It is in this region, where the field strength reaches the very high values of 10^{10} V m^{-1}, that the entropy effects and the electrostatic energy are localized. From these observations an important result can be deduced -- the interphase is at the same time an ionic as well as an electronic conductor.

An analogous concept may be seen to be implied on what was suggested earlier by Piontelli[18] and recently stressed by Malev[160], that the electrode/electrolyte interphase is a region where the principle of electrical neutrality is violated.

8. The Adiabaticity of Electronation

In electrodynamic processes, electron-transfer occurs under conditions which are beyond the conditions for radiationless electron tunneling, as presented in the literature. For example in Bockris' various works[2-74] on proton discharge reaction, the following condition is given --

$$-E_F + E_R - E_{Ad} - E_I + E_L = 0$$

where:

E_F - Fermi energy

E_R - Repulsive energy between proton and electrode metal

E_{Ad} - Adsorption of H atom on electrode surface

E_I - Ionization energy of the H atom

E_L - Proton solvation energy

(-) - helps the proton discharge process

(+) - opposes the proton discharge process

As discussed section IV,4, the above type of expression also suffer from the problem of potential energy equilibrium with its disregard for the dynamic nature of the electrode process. In fact, the term accounting for the kinetic energy of the incoming ion-atom is not included in that expression.

The constraint that the energies of the electron in the donor (parent atom of the electrode surface) and in the acceptor (incoming ion) must be equal, is still regarded as valid since, as anticipated, Galvanoluminescence phenomena will not be studied. However, the electron distribution among energy levels at the metal electrode surface, depends on its temperature (since the electrons for the electronations come from atoms of the surface), thus the electrons involved may have energies higher than the Fermi level. Therefore, the electronation process should be assumed to occur adiabatically according to Ehrenfest's definition which is usually stated as follows -- (from Messiah[167])

> "In the limit when the transmission time tends to zero, in the case of an infinitely rapid passage [*which is the case for electron exchange*] the dynamical state of the system remains unchanged."

That is, adiabatic processes are reactions in which a charge exchange occurs such that the time period of collision is greater than the time period of internal electronic motion. Such reactions occur without change in electronic quantum number, that is, they take place on a single electronic potential energy surface.

Consequently, the electrodynamic approach assumes that the effect on the energy of the active species, due to the electron-transfer act is negligible. As indicated earlier, the importance of the electron transfer is in that it determines the point in time and in space for the major discontinuity in electrode processes.

9. On the Negligibility of Adsorption Phenomena

The author of this thesis does not regard entities like adatom, adaion, embrios, etc., to be relevant under the operational conditions of live metal producing electrode processes as defined in section IV,A. Therefore, no comments will be offered on this subject, as it will become clear during the treatment that the role of the above type of sorption (ad and ab) can be neglected.

The adsorption interaction between water molecules and the metal electrode has been studied[168], among others, by Macdonald and Barlow[109] in connection with the determination of the dielectric constant value for the electrode/ electrolyte interphase region. Neglecting the association between water molecules forming the monolayer, in the inner layer model (one layer of solvent molecules hexagonally close-packed, charge free, physically adsorbed on the electrode by dipole image force) they calculated the "natural" field arising from the binding energy anisotropy, for various assumed conditions. The largest value of binding energy was obtained for the case where the monolayer dipoles are imaged on an infinite set of images in an equipotential plane on the other side of the layer -- this value was -1.4 kcal/mole, and the natural field strength was determined to be -1.52×10^{-8} V m^{-1}.

It seems, therefore, reasonable to assume that a field strength of 10^{+9} V m^{-1}, corresponding to normal values for electrode processes as discussed in section II,K, will disrupt any adsorption interaction involving water and metal electrode. Systems containing organic additives will not be studied. Only the adsorption of gaseous elements (H_2 and O_2) will be taken into consideration in view of the magnitude of the energies involved.

Further, the water molecules present in the layer near the cathode have just undergone the dehydration process, thus, they will still be in an excited state, i.e., Levich's solvent fluctuation reviewed in section II,G,2, and therefore, will not be able to establish adsorption interactions. Finally, the results of the experimental part of this thesis proved that in the case of the cathodic interphase the local temperature is far too high for adsorption processes to occur.

10. De-Excitation of Products

The energy obtained by the de-activation of the products of metal cathodic electrodeposition process is the single most important quantity of the electrodynamic model. This energy is the result of the additive contributions of the type of electrode reaction and of the irreversible nature of the electrode process; that is of the dynamic occurrence of the heterogeneous reactions at the electrode/electrolyte interphase.

We have seen during the literature survey, numerous instances where the concept of this energy of products de-activation has been mentioned or at least implied. For a better recollection they have been listed here below --

Bockris and Srinivasan in section II,E
Hush in section II,G,2
Reynolds and Lumry in section II,G,2
Laidler and Tweedale in section II,H
Vagramyan et al., in section II,O,3
Thouvenin in section II,O,7
Yahalom and Zahavi in section II,O,8
author's M.S. Thesis in section II,P
Kushner in section II,Q,4

However, no detailed analysis of this phenomenon could be found in the literature.

All of the de-activation energy is released at the interphase and is transferred in both the electrode and solution directions. The flux of energy which is dissipated into the metal side of the interphase is defined "Excess Energy" and as far as this investigation is concerned, is the most important quantity since, in the form of heat, it affects the physico-chemical properties of the product of the electrode reaction -- the electrodeposited metal.

The remaining part of the de-activation energy is transferred in the direction of the electrolytic solution, where it is carried away by the exchange of excited water molecules with the bulk, and actually helps the ion dehydration process through a mechanism similar to Levich's solvent fluctuation, reported in section

The de-activation energy of the products of metal anodic electrodissolution processes is mostly associated with the hydrated ion complex. In addition, very few authors predict or even speculate on the existence of a region at the metal side of the interphase, being at an energy density lower than the rest of the cell, as the electrode process occurs. As reviewed in section II,F only Eastman[165] discusses and develops a treatment for what we will call "Anodic Cooling" effect. Then Kushner[136] speculates on the existence, for thermodynamic reasons, of a 'refrigeration effect' for which however, he had no evidence. Finally, the writer, in his M.S. Thesis[86] suggested the existence of the anodic cooling in order to explain various phenomena occurring in titanium electrorefining.

This last statement precisely indicates the reason why the electrodynamic model has been introduced. The theoretical and experimental confirmation of the non-isothermal behavior of electrochemical processes, namely the existence of the cathodic heating and anodic cooling effects, permits the explanation of most of the poorly understood phenomena indicated in section

11. The Method for Estimating the Values of the Cathodic Heating and of the Anodic Cooling Effects

The method based on the arbitrary separation of electrical and chemical contribution in the electrochemical potential of a reacting species has already been discussed in section II,E with the conclusion that this procedure is not appropriate for the study of electrochemical processes far from equilibrium. Moreover, we have seen in section III,10 that the phenomenological relations for irreversible processes do not seem to be applicable to electrode processes.

In section II,H we have seen that Laidler and Tweedale[73] used Karplus linear collision threshold energy data in the calculation of activation energy. Since, at the present time, this type of data are only available for H_2 and D_2 systems, in order to attempt a solution to the problem of estimating the values of the cathodic heating and of the anodic cooling, without violating the principle of the integrity of the electrochemical potential, the direct measurement of the de-activation energy of the anodic and cathodic products independently, seems to be the only method available. In addition, the use of the Georgian scale (see section II,O,2 permits the conversion between the values of energy density and temperature.

CHAPTER V. DEVELOPMENT OF THE ELECTRODYNAMIC MODEL

0. Introduction

The conclusion of the previous chapter left little hope for an analytical calculation of the promotional and de-excitation energies by the use of established methods. However, one of the aims of this thesis is to attempt the construction of a model which will permit the numerical calculation of those energies. It will be therefore shown that the embodiment of the various aspects of electrochemical kinetics, which were discussed in the previous chapter may be accomplished by one model which represents a closer compromise to physical reality than has been established hitherto.

It may be appropriate at this juncture to comment on the choice of the name 'electrodynamic' which has been borrowed from Sommerfeld's classical book by this title in order to stress that this model is concerned with the energies of far-from-equilibrium electrochemical processes rather than with potential energies associated with equilibrium conditions.

1. Species Interactions

What follows is a qualitative description of the possible interactions among species having a part in a electrode process. This is a necessary initial step leading to the quantitative determination of the relative significance of the interactions.

The cathodic deposition of a metal from aqueous solutions could be thought of as resulting from various interactions taking place in two successive time periods. The first time period, before the electron transfer has occurred, involves the following types of interactions --

- attraction between metal ion and water molecules (hydration energy)
- attraction between the parent metal atom of the electrode surface and the electron (electron extraction energy)
- attraction between metal ion and the electron (ionization energy)
- attraction between the hydroxyl group produced by hydrolysis and the metal ion (hydroxide formation)
- interaction between the metal electrode and the metal ion (adsorption energy, adion)
- interaction between metal ion and organic molecules at the surface of the electrode (addition agent effect)

The electron-transfer marks the change in identity of one of the species (ion-atom), thus all the interactions now become modified. This electron-transfer is assumed to be adiabatic as will be described later. The second time period, which begins as soon as the electrons are transferred to the ions, involves the following interactions, which superimpose onto the energetic state of the newly formed atoms --

- repulsion between metal atoms and water molecules (hydrophobic)
- attraction between metal atom and electrode surface (short range energy)
- attraction between metal atom and the electrode surface (adsorption energy, adatom)
- interaction between metal atom and organic molecules at the electrode surface (addition agent effect)

2. Geometrical and Structural Arrangement

An electrode process can be thought as happening within a volume interphase, which looks more like a confused multilayer than the traditional sharp double layer. Strictly speaking, this interphase is a non-homogeneous region with constantly changing chemical identity and energy of the species making up this region. However, for the purpose of clarity, a multilayer composed of five phases will be assumed to appropriately describe the electrode/electrolyte transition region, as sketched in Fig. V,1 where the metal electrode is pictured at the left while the electrolytic solution at the right. The idealized planar interfaces between phases are labelled as follows --

(M/S) - interface between metal bulk and selvedge

(S/E) - interface between selvedge and electronation interphase

(E/D) - interface between electronation interphase and diffuse, Wien plane

(D/B) - interface between diffuse and electrolytic bath

(ES) - cathodic electron surface

(HP) - anodic hydration point

(MB) - electrode metal bulk

(S) - selvedge phase

(EN) - electronation interphase

(D) - diffuse phase

(SB) - electrolytic solution bulk

(EP) - electronation point

(IC) - incoming ion position

3. Identity of Species Present in Each Phase

Starting from the electrode side and proceeding towards the electrolytic solution region, in Fig. V,1, we consider the metal bulk, which is a homogeneous phase composed of metal atoms with constant physico-chemical properties. On approaching the metal/electrolyte transition region, ideally we meet an interface (M/S) between the uniform bulk metal and the electrode surface region. To this volume interphase

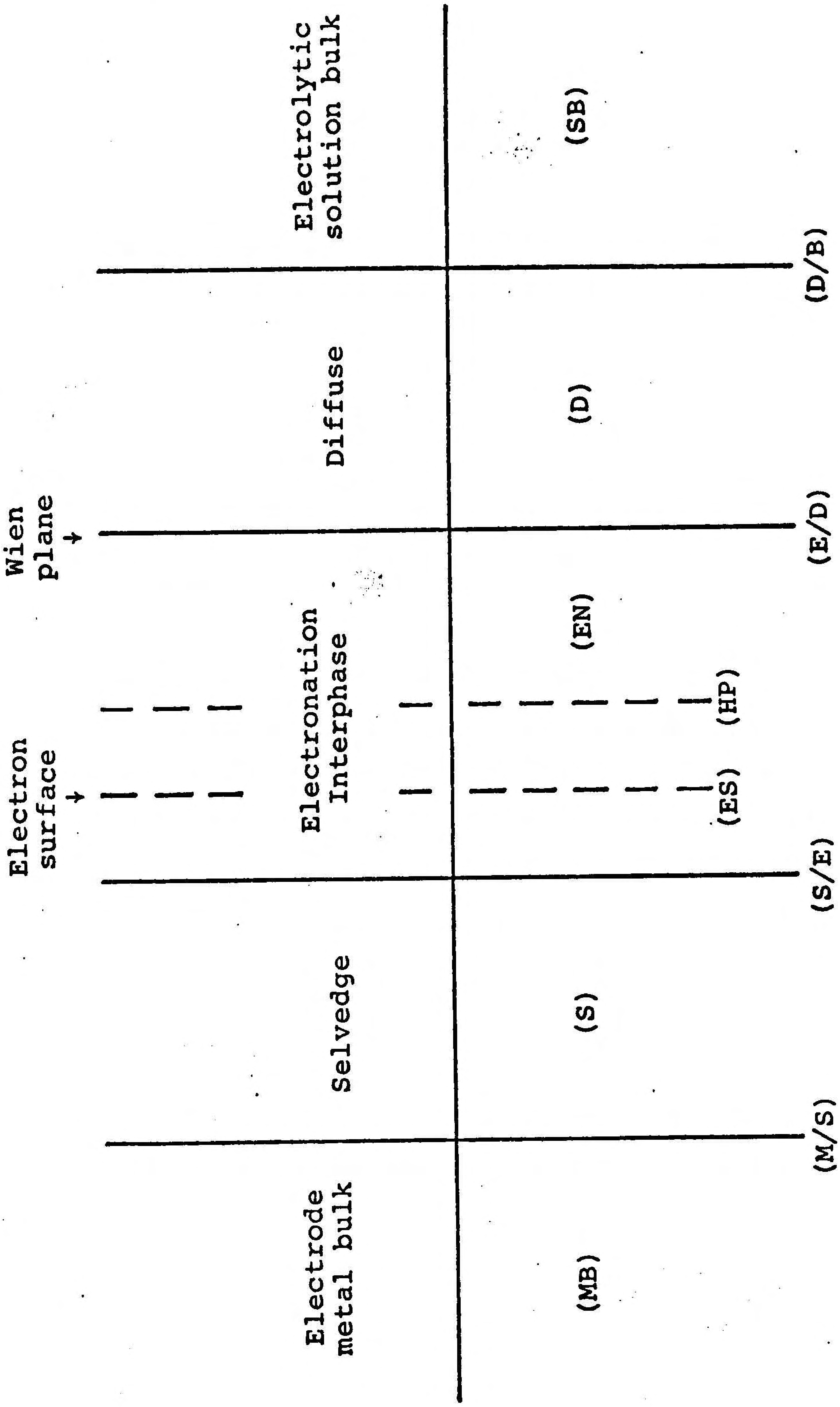


Fig. V,1 - One dimensional arrangement of the electrode/electrolyte interphase.

which is non-uniform in regards to the constituent atom's energy and crystal structure, the name "selvedge" has been assigned.

Next we have a most important boundary, the interface (S/E) between the selvedge and the electronation interphase. This electronation interphase is the most complex element of the metal/electrolyte transition region. It is formed of neutral species (atoms just formed), of neutral species having an oriented dipole, and of ionically dissociated species. No hydrated complexes are present in this phase, as will be discussed later.

Now we consider the interface (E/D) ideally dividing the electronation interphase from a diffuse phase, which is a region similar to the traditional diffuse layer but characterized by the fact that, not only is the metal ion concentration not uniform, but also, and most important, the symmetry of the hydrated ion complexes present in various points in this phase, has different degree of distortion. This fact led us to assign to the (E/D) interface the name of "Wien plane" as will be discussed later.

Finally, this diffuse region is ideally separated from the bulk of the electrolytic solution by the interface (D/B), which marks the point beyond which the distortion of the hydrated complex begins to appear when proceeding from the solution toward the electrode. The structure of the electrolyte is such that the water molecules are in number sufficient only to provide the first hydration shell around each ion; or, in other words a structure approaching that of molten salts electrolytes. This corresponds, typically, to solutions with concentration larger than one molal.

4. The Selvedge Region

The name "selvedge", borrowed from solid state physics[41] has been assigned to the region between the metal bulk and the electronation interphase. This selvedge phase is characterized by being made up of metallic atoms that have energies and spatial arrangements different from those of the bulk metal. Actually, a gradient in these properties exists across the selvedge, with the atoms having higher energy at the right end of the selvedge (at the boundary with the electronation interphase) while the atoms of the lower energy (tending toward the bulk value) are on the left at the metal bulk interface.

This selvedge is a dynamic region; that is, it exists because the electrode reaction occurs. As for an order of magnitude, its thickness is at a minimum value (> 10 Å), for a given metal electrode, when no net current is generated (or nullified), and increases with increasing current density.

It must be stressed that the selvedge thickness reaches a minimum value that is always larger than zero (always finite), because of the existence of the exchange current which provides the dynamism at the electrode/electrolyte transition region.

As for the spatial arrangement of the atoms, the selvedge is assumed to have a paracrystalline structure of varying degree of ordering; ranging from a highly ordered lattice at the left-hand side to an increasingly disorganized structure, on proceeding toward the electronation interphase. This degree of disorder increases with current density, the structure of the right-most atomic layers approaching that of molten metal. In order to clarify the meaning of this last statement, which may immediately generate the question of the difference on the electrode process behavior, of having a solid substrate as compared with a liquid one, consider the following -- The work of Hoseman, et al.[87] was reported in section II,K. It gives radial-distribution functions for molten metals out to a distance of 25 Å, which corresponds to an fcc lattice having a lifetime of 10^{-11}s. If we recall that Eyring's rate theory predicts a lifetime of 10^{-14}s for the ions in the transition state, we can see that for the electrode processes there is no difference between having the bulk of the electrode in liquid or solid state, since the transition-state ions see the selvedge as a steady structure during the reaction time.

The high-energy paracrystalline structure of the right-most atoms of the selvedge is a result of the process of dissipation of the excess energy as defined in section This energy dissipation in the direction of the bulk will occur faster along the reaction coordinate the larger the plane density of the atoms forming the selvedge.

The above considerations are summarized in Fig.V,2 sketched for the case of cathodic heating effect. The local system composed by selvedge and portion of metal bulk is the analogous of Bockris' and Reddy's "Electrodics". The energy density gradient determines the thickness of the selvedge.

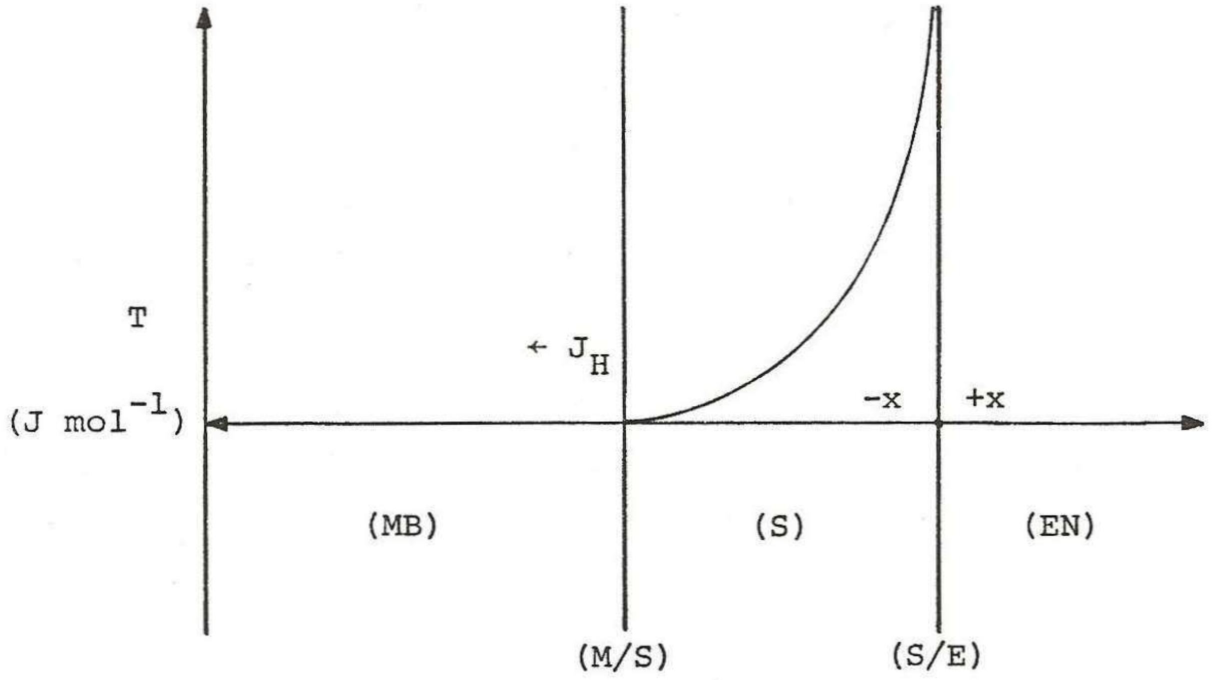


Fig.V,2 - Semi-infinite electrodic system.

The heat flows from the high temperature electronation/ selvedge interface (S/E) to the lower temperature metal bulk.

Heat absorbed by the system from (EN) is considered to be positive, and Fourier's law can be applied: $J_H = -k \nabla T$, since the heat flux vector points in the direction of decreasing temperature. Thus, the externally imposed electric field generates an electron flux which can assist or oppose the normal conduction of heat.

In summary, the shape of the energy density gradient and the value of the virtual temperature depend upon the following --

(1) current density, i.e., energy flux,

(2) heat transfer characteristics of the electrode metal,

(3) heat transfer characteristics of the species present in the electronation interphase, and their exchange rate with the species present in the solution bulk.

5. Electron Surface

From the above considerations on electron-surface reaction, the following assumption regarding the location of the electron plane given below seems to be realistic.

Since the velocity of electronic motion is about 10^3 times faster than the ionic motion[158], we could consider (Born-Oppenheimer approximation) the electron transfer as taking place between species which are at a fixed location during the transfer reaction time. Conversely, following the species motion in the electrode/electrolyte region, we can assume that, for a given set of electrochemical conditions, the electrons are available at all times at a plane located within the interphase.

About the possibility of estimating the availability of enough electrons at the electron surface for the quasi-equilibrium assumption, Bockris and Reddy[2] offer a simplified derivation, which avoids the complexities of a complete development of the Fermi-Dirac statistics, for the determination of the number of electrons having the Fermi energy, striking the surface of a metal electrode from inside. The number of electrons with Fermi energy available at the electron surface per second and per square meter is given by --

$$n(E_F) = \frac{4\pi\, m_e\, (\kappa T)^2}{h^3}$$

where:

m_e - electron rest mass (9.1095×10^{-31} kg)

κ - Boltzmann's constant (1.3806×10^{-23} J °K^{-1})

h - Planck's constant (6.6262×10^{-34} J s)

This number comes out to be, for 300°K of the order of 10^{30} electrons m^{-2} s^{-1}. This also follows from the treatments of electron gas within an electronic conductor available in the literature. For example, a most recent one by Abrikosov[157] deals with an isotropic Fermi fluid of quasi-particles which is valid for temperatures up to 10^4°K.

In the absence of external electric fields (superimposed voltage difference between the inside and the outside of the electronic conductor, ab- and adsorption, or covalent/ionic bond with species at the surface of the conductor) this electron plane can be thought of as being located at the external tangent of the outermost electronic shell of the last atom of the surface. The effect of external fields is to shift this electron surface from the location just described. In the case of cathodic mode, the electron surface is moved toward the electrolytic solution, while for the case of anodic mode, the surface is pulled into the metal electrode.

6. The Electron Extraction Energy

This terminology has been introduced by Piontelli[1] to replace the term "work function" in the definition of the energy required for the emission of an electron from the highest occupied energy level of a conductor. This new term is regarded as more appropriate both because it eliminates the possibility of confusion with Helmholtz energy function sometimes called work function in thermodynamic treatments, and because the term electron extraction energy (from here on referred to as EEE) is much more informative.

In electrochemical processes this energy to extract electrons from atoms at the surface of electrodes is supplied to the system by applying an overpotential, which has the effect of shifting the free electron gas outward from the electrode surface for cathodic mode, and inward for anodic. The amount of the energy involved is not a constant, as in solid state electron emission processes, but it varies with the distance of separation between the incoming ions and the electrode surface. It is a variable whose value depends on the rate of the electrode process, ranging from approximately zero when the ion is adsorbed (in Van der Waals contact) on the atoms of the electrode surface, to its maximum value which corresponds to the formation of hydrated electrons; as reported in section II,M,4 Kenney and Walker gave a value of -2.7 eV for $e^{-}_{(aq)}$ standard potential, which is considerably smaller than the values of physical work function as reviewed in section II,N. The assertion that its minimum value can be zero is in agreement with the fact that no treatments of the problem of the evaluation of the EEE for a reaction carried out in chemical mode could be found in the literature.

The most important aspect of EEE is that this energetic expenditure does not result in a de-activation energy, but only provides the supply of electrons for the transfer reaction. This follows from the concept of adiabaticity of electronation discussed in section IV,8.

We can visualize the effect of the different magnitudes of the physical work functions for various metals, in what, for live electrochemical processes under the same value of overpotential, the larger the value of the work function, the closer to the cathodic selvedge the electron surface will be. Conversely, metals with low work functions possess electrons with low kinetic energy in the Fermi level, thus low surface potentials, and further away the electron surface will be, for the same overpotential. This is in agreement with Trasatti's suggestion mentioned in section II,N.

As indicated earlier (section IV,4) the value of EEE is a function of selvedge temperature, interphase energy density, and possibly of pressure in the interphase. In the development of the electrodynamic model the EEE curve will be calculated as a function of distance from the valence shell of the first layer of atoms at the selvedge.

7. Electron Energy and Potential Energy

The concept of the energy and potential energy of electrons will be developed in analogy with the general treatment for charged particles discussed in section

Consider an electrolytic refining cell in which the reaction $Cu°_{(anode)} \rightarrow Cu°_{(cathode)}$ occurs. Gibbs' thermodynamics states that the value of the overall reaction free energy change must be negative for the process to occur; thus, the fundamental relation $\Delta G = nF\eta$ says that when no overpotential is imposed on the cell the electrorefining reaction will not go. The reaction will occur in the direction indicated for $\Delta G < 0$, which implies $\eta < 0$.

This means that the electron-metal atom system potential energy decreases from anode to cathode across the electronic part of the electrochemical circuit, as it is sketched in Fig.V,3. On the same Fig.V,3 the potential energy curve for the electron-metal ion system is superimposed across the ionic part of the electrochemical circuit.

In analogy with what it has been indicated in section when the potential energy of the electron-metal atom system decreases, the energy of the electrons increases. This is precisely the physical meaning of the location of the electron surface at some distance from the metal atoms of the cathodic selvedge, and it is in agreement with the concept of electron activity, which is high at the cathode and low at the anode.

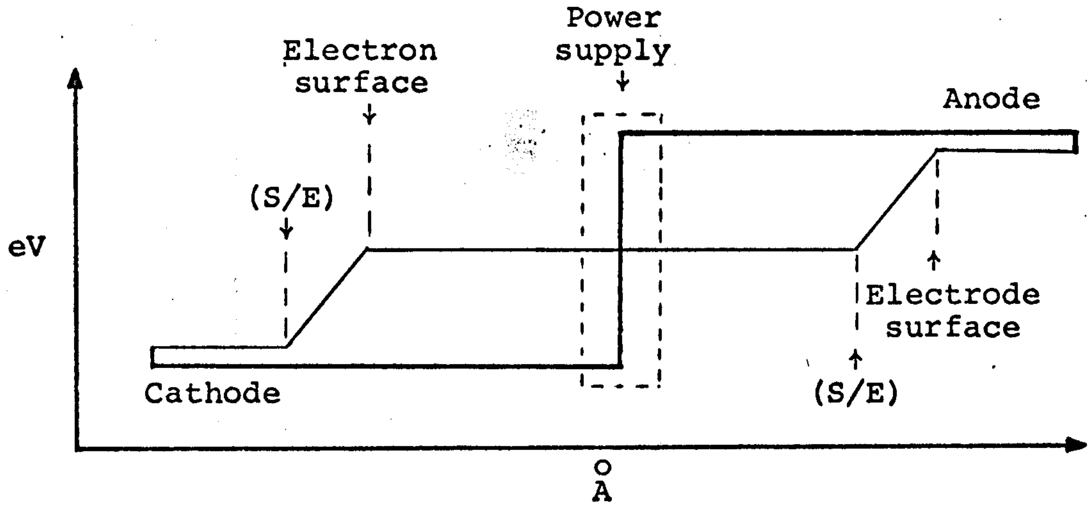


Fig. V,3 - Potential energy curve for electrons. The thick line refers to the electron-metal atom system, while the thin one refers to the electron-metal ion system.

8. The Electronation Interphase

This phase of the electrode/electrolyte region can be considered as the seat of emf. That is, when applying an external potential difference on the electrode/electrolyte region, the electron potential energy gradient is assumed to exist only within the electronation interphases of the two electrode/electrolyte regions forming the electrolytic cell, and not in any other region of the system.

It is defined as the region between the last atom layer of the selvedge and the Wien plane, and it contains the electron surface. The ion electronation occurs within this interphase, and more precisely between the electron surface and the Wien plane.

Under dynamic condition of electrodeposition, the values of the electric field strength, pressure, and temperature (energy density) within this phase are at very high levels, as was pointed out during the literature survey and as will be discussed in the numerical application in section VI.

9. The Electronation Point

The Electronation point is located within the electronation interphase, between the electron surface and the Wien plane. It is defined as the point where the individual electric field strength between the electron and the electron surface and the parent atom at the selvedge, becomes infinitisimally smaller than the electric field strength between the same electron at the electron surface and the incoming ion.

We can assume to be able to reason in terms of distances measured with respect to a fixed point in the metal bulk; thus when $[(ES) - (S/E)] > [(IC) - (ES)]$

where:

(ES) - electron surface

(S/E) - selvedge/electronation interface

(IC) - incoming ion position

the electron is instantaneously transferred to the incoming ion. The position of the incoming ion at this instant in time is the location of the electronation point.

10. The Wien Plane

The Wien effect, which was described in the literature survey (section II,M,2) plays a most important role in the electrodynamic model. It occurs when the electric field strength between the hydrated ion complex and the electrons at the electron surface is larger than 10^6-10^7 V m^{-1}. This value is assumed to be a constant for each ion in aqueous systems, within the range mentioned, and for a given externally applied potential difference, it determines the distance, from the electrode surface, where the Wien effect occurs. Consequently, this location will be called the "Wien plane".

In order to gain a magnitude of that distance, let's externally apply to an electrolytic cell a potential difference of 0.2 V, and assuming an equal partition between the two electronation interphases, we have a 0.1 V across either one; this results in: $(10^{6}V/10^{0}m) = (10^{-1}V/x\ m)$ a distance between 100 and 1,000 Å, which will increase upon increasing the externally applied potential difference.

However, the Wien plane distance from the electrode surface, similarly to the selvedge thickness, will not go to zero for zero externally applied potential difference, but will reach a minimum finite value which is determined by the Galvani potential characteristic of the electrode/ electrolyte couple, which in turn sustains the exchange current.

In summary, the Wien plane marks the location of the end of the life of the hydrated ion complex as the entity that was defined in section II,L,2, and its configuration at this point can be imagined as sketched in Fig. VI,1. Moreover, the Wien plane marks the location where the ion starts to accelerate from the hydrated complex drift velocity of 10^{-6} m s^{-1} to a linear velocity toward the electron surface of the order of 10 m s^{-1}.

11. Qualitative Description of Metal Deposition and Dissolution in Terms of the Electrodynamic Model

The thermodynamic cycle for metal cathodic deposition in terms of the electrodynamic model and with reference to the terminology introduced in section V,2, can be qualitatively summarized as follows --

a) $Me(H_2O)_6^{++}{}_{(SB)} \rightarrow Me^{++}\cdot 6H_2O_{(D)}$

is the first step involving the rearrangement energy absorbed by the hydrated system when crossing the interface (D/B) in going from the bulk to the diffuse region; (D/B) is the point at which, because of the increased electric field strength between ion and cathodic electrons, the hydrated complex loses its spherical symmetry, and becomes increasingly distorted during its drift toward the electrode. The ion being stretched to the left and the hydration molecules toward the right;

b) $Me^{++}\cdot 6H_2O_{(D)} \rightarrow Me^{++}_{(E/D)} + 6H_2O_{(E/D)}$

which represents the de-hydration energy absorbed and transformed into potential energy stored within the complex, up to the Wien plane (E/D) at which the ion is liberated from the attraction of the water molecules;

c) $2e^-_{(MB)} \rightarrow 2e^-_{(S)}$

accounts for the Peltier effect involving absorption or release of heat at (M/S), when the electrode substrate (the bulk metal) has a chemical identity different from the metal being deposited, thus forming the selvedge.

d) $2e^-_{(M/S)} \rightarrow 2e^-_{(S/E)}$

which accounts for the Thomson effect, since the selvedge is predicted to be at a higher temperature than the bulk metal. As the electrons arrive from the cold metal bulk flowing to the hot selvedge surface layer, they increase their potential energy by absorbing energy by heat transfer from the selvedge;

e) $2e^-_{(S/E)} \rightarrow 2e^-_{(ES)}$

represents the electron extraction energy, as discussed in section , for the electrons to reach the electron surface;

f) $Me^{++}_{(E/D)} \rightarrow Me^{++}_{(EP)}$

where the metal ion potential energy is transformed into kinetic energy during the deionization process;

g) $Me^{++}_{(EP)} + 2e^-_{(ES)} \rightarrow Me^\circ_{(EP)}$

when the ion has reached a distance from the electrons at the electron surface equal to the distance between these electrons and the atom at the selvedge surface, electronation occurs according to the above;

h) $Me^\circ_{(EP)} \rightarrow Me^\circ_{(S/E)}$

the newly formed metal atom continues to translate with the amount of kinetic energy the ion was able to obtain from the conversion of its de-ionization potential energy. This amount of kinetic energy can be decreased by collision with species present at the electrode surface (organic additives, metallic and non-metallic impurities, etc.). However, it is also increased by the conversion of the deatomization potential energy into kinetic energy. The final value of kinetic energy that the atom has at (S/E) is the excess energy:

i) $Me°_{(S/E)} \rightarrow Me°_{(S)}$

finally, the excess energy is transformed into heat at the selvedge;

j) $6H_2O_{(E/D)} \rightarrow 6H_2O_{(D/B)}$

on the solution side, the water molecules of previous hydration convert their potential energy into energy which they transfer to other molecules, thereby enhancing the process of rearrangement and dehydration of incoming ionic compleses.

Therefore, the overall cathodic electrode reaction for metal deposition, which is the equivalent to the opposite of the reaction which completes the cycle, is:

$$Me(H_2O)_{6\ (S/B)}^{++} + 2e^-_{(MB)} \rightarrow Me°_{(S)} + 6H_2O_{(D/B)} + EE + SF \qquad V,$$

where the excess energy (EE) term contains:

1) potential energy difference between $Me^{++}_{(E/D)}$ and $Me°_{(S)}$;
2) Peltier effect;
3) Thomson effect;
4) collision energy with species at the electronation interphase
5) entropy difference between the newly formed atom at EP and the same atom at the selvedge.

and where the solvent fluctuation term, SF, contains the potential energy difference between $6H_2O_{(E/D)}$ and $6H_2O_{(D/B)}$. It is important to note that not only the species extitation energy has been considered but the entropy changes of both the ionic systems and the surroundings has been accounted for along the lines of Eastman's theory, as reviewed previously.

Analogous to metal deposition, the thermodynamic cycle for metal anodic dissolution in terms of the electrodynamic model and again referring to section V,2 for the terminology, can be summarized as follows --

a) $Me^{\circ}_{(S/E)} \rightarrow Me^{++}_{(S/E)} + 2e^{-}_{(ES)}$

the electron surface during anodic dissolution is pulled inside the selvedge. This is complementary to the electron extraction energy, and results in metal surface ionization;

b) $Me^{++}_{(S/E)} \rightarrow Me^{++}_{(S/E)}$

this indicates the process of electron internal rearrangement since the electrons remaining in the newly ionized species are balanced with the same positive nucleus charge, and thus are pulled to orbit closer to it. The ionic radius is smaller than the atomic radius without the valence shell;

c) $2e^{-}_{(S)} \rightarrow 2e^{-}_{(MB)}$

for the Peltier effect;

d) $2e^{-}_{(ES)} \rightarrow 2e^{-}_{(M/S)}$

for Thomson's effect;

e) $Me^{++}_{(S/E)} \rightarrow Me^{++}_{(HP)}$

the potential energy of repulsion between metal ion and the selvedge is converted into kinetic energy translating the ion toward the solution with decreasing acceleration up to the hydration point at which the water molecules attractive interaction begins to occur. This process leaves the selvedge at lower energy density;

f) $Me^{++}_{(HP)} + 6H_2O_{(D/B)} \rightarrow Me^{++}\cdot 6H_2O_{(E/D)}$

the hydration potential energy is converted into kinetic energy for translation of the metal ion and the water molecules relative to each other, and into energy which is transferred to other water molecules;

g) $Me^{++}\cdot 6H_2O_{(E/D)} \rightarrow Me(H_2O)_6^{++}{}_{(D/B)}$

finally, the rearrangement potential energy is also converted into energy transmitted to other water molecules and the metal ion hydrated complex becomes a stable part of the solution bulk.

In summary, the overall anodic electrode reaction for metal dissolution is:

$$Me^{\circ}_{(S/E)} + 6H_2O_{(D/B)} \rightarrow 2e^-_{(MB)} + Me(H_2O)_6^{++} + \bar{SA} + AC \qquad V,2$$

where the term SA, contains:

1) the energy converted from potential energy of hydration;
2) the rearrangement energy;

and the anodic cooling term AC, which represents the energy change at the electrode side of the interphase, contains:

1) difference in potential energy between $Me^{++}_{(S/E)}$ and $Me^{++}_{(HP)}$ -- that is the energy extracted by the outgoing ion;
2) Peltier effect;
3) Thomson effect.

It may be concluded that not only the species' internal energy changes must be considered but also their dynamic distribution in space. The importance of the entropy change contribution to the overall energy change will be discussed in the next section.

12. Dynamic Entropy Distribution Generating Cathodic Heating Effect and Anodic Cooling Effect

After the discussions of the previous sections it seems to be useful to reiterate what already has been indicated in section IV,5, that interference between irreversible processes is possible only when they occur in the same region of the system.

In an electrolytic cell we have two separated electrode/electrolyte interphases which have as the only connection between them the electrons in the electronic part of the electrochemical circuit. Under live operational conditions the entropy change in each interphase will be the result of the contributions of the internal production and of the exchange with their respective neighboring phases. Therefore, the two irreversible processes occurring at the two electrolyte/electrode interphases, and composing the overall reaction, will not interfere with each other. This inherently electrochemical feature has been discussed in section Consequently, the energy changes occurring at the two electrodes can be analyzed independently.

The first consideration we can make in the analysis of the entropy changes at the interphase under cathodic mode - metal deposition - is the following --

(1) the ions gain energy during the dehydration process in the form of increased vibrational amplitude of interaction with water molecules of their primary shell of hydration (entropy production in solution);

(2) the ions accelerate within the interphase in the direction of the electrode surface (entropy transport from solution into the interphase, and entropy production within the interphase) leaving behind a region of lower energy density if the heat of transport and/or new ions cannot be immediately and completely supplied to this region;

(3) finally, after having received their neutralizing electrons provided by the externally imposed potential difference, the atoms reach the electrode surface and lose their kinetic energy by transferring it to the metal electrode (entropy transport from the interphase to the metal electrode and production at the electrode surface).

Thus, we can see that in each of the phases we have an entropy production and an entropy transfer to a neighboring phase. Now, the comparison between the values of entropy production and entropy transferred for each individual phase is a most important point, since it will indicate the value of the energy density in each phase resulting from the electrode reaction.

Summarizing, at the metal electrode surface under cathodic mode, the entropy produced by the last step of the electrode reaction is transferred to the electrode itself from the neighboring phase, and this results in a net energy density increase. This is an additional energy change besides the de-excitation of the species considered in the last section. Then, unless the heat of transport and the kinetic energy of the atom are removed from this region as sensible heat, thus decreasing the entropy of the atoms in the electrode surface, this region will heat up. Further, the solution side of the interphase which is left at a low energy density, will become uniform at a much faster rate than in the solid metal side of the interphase due to the convective mass transfer process in this liquid phase.

Consequently, the occurrence of a cathodic heating effect at the metal electrode surface seems a reasonable conclusion from the above considerations.

Analogous considerations may be attempted for the case of anodic mode at the interphase - metal dissolution --

(1) the free electron gas is displaced toward the inside of the metal electrode by the externally imposed potential difference, leaving ions* in a state of strong repulsive potential energy interaction (entropy production);

(2) then, the ions will convert their potential energy into kinetic, accelerating (entropy transported and produced) in the interphase toward the solution, leaving behind a region of low energy density;

(3) finally, the ions interact with the water molecules and lose their kinetic energy by transferring it

---

* actually, positively charged transient species, not yet ions, as it was discussed in the previous section.

to the water molecules (entropy transferred from interphase to solution and production in the solution).

In analogy with the cathodic mode, here again, we can state that in each of the phases we have entropy production and entropy transport to neighboring phases, and the algebraic summation of the two will indicate the energy density change in each phase resulted from the occurrence of the electrode reaction.

Summarizing, the metal electrode surface under anodic mode after the metal dissolution has occurred, is left at a low energy density value, since it has provided the repulsive energy to accelerate the ions and it has lost the molar entropy associated with the dissolving ions; thus, unless energy can be supplied in the form of sensible heat, this region will cool. Further, the entropy produced by the final step of the electrode reaction is transferred to the solution side of the interphase. Thus, a net energy density increase will result if the heat of transport, the kinetic energy of the ions, and the hydration energy cannot be removed. However, again, since this region is a liquid phase, the mass transfer processes will equalize the energy at a much faster rate than in the solid metal side of the interphase.

Therefore, here also, the occurrence of an anodic cooling effect at the metal electrode surface, under dynamic live condition, seems a reasonable conclusion from the above considerations.

CHAPTER VI. NUMERICAL ANALYSIS OF THE MECHANISM OF COPPER DEPOSITION WITH THE ELECTRODYNAMIC MODEL

A. INTRODUCTION

After the qualitative considerations presented in the previous chapters, an analysis of a real electrochemical system in terms of the electrodynamic model in order to obtain numerical useful results will be attempted. The calculation of the values for the variables indicated in the development of the electrodynamic model will be performed for representative sets of electrochemical conditions. In particular the following type of data are sought -- the location of the Wien plane, of the electronation point, and the energy the newly formed atoms have at the selvedge.

From the list of the possible two-body interactions indicated in section V,1 for the period preceeding the electronation, we will choose the ones which are applicable to the half reaction for the reduction of the cupric ion from an aqueous electrolytic solution of the type described below.

First, the hydration interaction between the ion and its water molecules of primary shell is energetically important, and it will be used to determine the location of the Wien plane as a function of the overpotential. The second important interaction is that between the ion and its neutralizing electrons, which involves the de-ionization energy and is the natural driving force for the process. The third interaction occurs between the copper metal atoms at the selvedge and the electrons at the electron surface. This is the electron extraction energy which was discussed in section V,6 and it will be used to determine the location of the electron surface as a function of the overpotential.

As indicated in section IV,9, the adsorption type of interaction involving species such as adion, adatom, etc., will be considered not relevant to this process. Regarding the role played by the hydroxylion, the condition and the composition of the electronation interphase (as indicated in section VI,B), its activity in strongly acid solutions, and the value of its affinity for copper are such that the assumption that it is of only secondary importance is regarded as reasonable. Further, no organic molecules are present in the electrolyte.

Thus, the electrode process during the first time period (before electronation) is assumed to occur as a result of the three independent two-body interactions indicated. The combination of the values of the energies involved in the above interactions will permit the determination of the location of the electronation point and of the energy which the newly formed atom has at that point.

Soon after, the second time period of the electrode process begins during which the important interactions are the following --

First, the repulsion between the atom and the excited water molecules in the interphase, as a function of, among other parameters, the pressure in the electronation interphase, tending to drive the new atom out of that region. Now follows the attraction between the atom and the metal surface which involves the atomization energy, and is a function of the selvedge temperature.

The addition of these latter two energies to the energy which the newly formed atom has at the electronation point, will determine the value of the excess energy at the selvedge. Strictly, the energetic expenditure for translation of the atom from the electronation point to the selvedge should be deduced from that value. However, since it is assumed to operate in the absence of species which accumulate on the electrode surface (organic additives), the above is a realistic approach.

B. DE-HYDRATION

1. Structure of a Concentrated Electrolytic Solution

As indicated earlier, this electrode process originates from a bulk electrolytic solution whose composition is in the range of ionic concentration generally used in industrial practice. Since no theory on the structure of concentrated aqueous solutions appears to exist at present, a structure based on the existence of hydrated ion complexes is calculated. This was done in order to check the statement of various authors[85 93], cited in section II,K, that the structure of aqueous solutions in the neighborhood of saturation, resemble ionic melts.

Thus, consider the following composition which may be regarded as representative of industrial specification:

1,000.0 g	H_2O	55.55 mol
159.6 g	$CuSO_4$	1.0 mol of each Cu^{++} and $SO_4^=$
196.0 g	H_2SO_4	2.0 mol of $SO_4^=$ and 4 mol of H^+

As pointed out in section II,L,3, no reliable value of hydration number exists. However, the hydrated complex configuration which is most mentioned in the literature[96] is the hexahydrated single ion. Thus, this configuration will be assumed to represent the entities present in the type of solutions indicated above.

Assuming this configuration, we can see that 6 water molecules are associated at any instant in time with each Cu^{++}, and 6 also with each associated $SO_4^=$ (being energetically equivalent to Cu^{++}). Moreover, there are another 12 molecules of water associated with $SO_4^=$ introduced by the sulfuric acid, and 1 for each of the 4 H^+, which form H_3O^+. Consequently, in this situation, 28 H_2O molecules out of a total of 55.55 are tied up with ions present in solution. The remaining 27.55 water molecules are not in number sufficient even to provide a complete secondary hydration shell, let along being left as 'free' water. Therefore, this structure indeed resembles an ionic melt, and its energetics will be treated accordingly.

2. Hydration Potential Energy Function

As indicated in the previous section, the ionic hydrated complex will be assumed as containing, in its bulk configuration, six water molecules in octahedral configuration forming its primary shell of hydration, as sketched on the left of Fig. VI,1. The remaining molecules of water will be regarded as having a negligible effect on the energy of the hydrated complex system, and will thus be considered as sort of spacers to help the relative translational motions of the complexed ions.

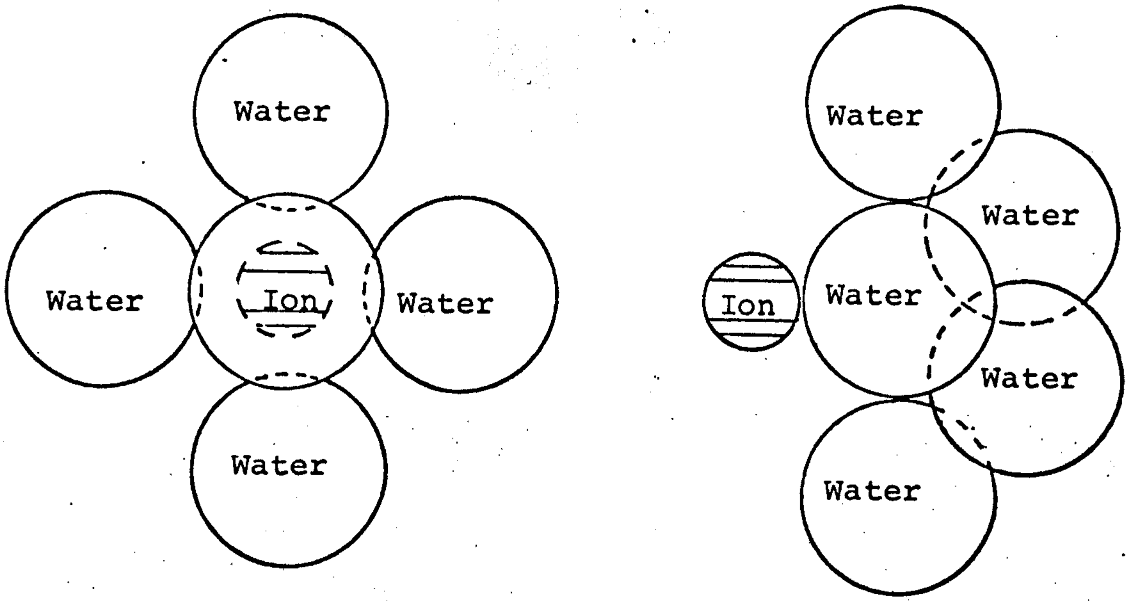


Fig. VI,1 - Geometrical configuration of the ionic hydrated complex, in the bulk of the electrolyte (left) and at the Wien Plane (right).

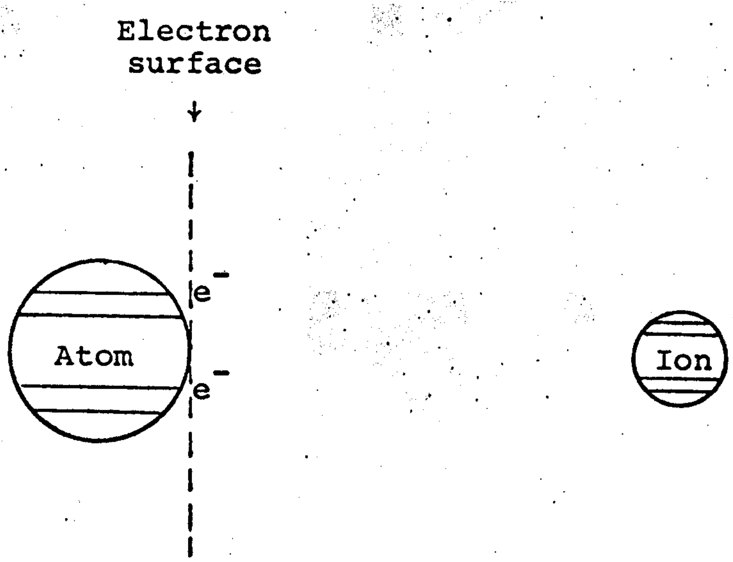


Fig. VI,3 - Analogue for de-ionization system.

Several authors (Bockris[2], Levich[44], Herzfeld and Griffing[169], J.C. Polany[33]) have used or indicated that it is satisfactory to use the Morse function to describe the interactions between species other than gaseous. This function will be used here too, to describe the characteristics of the two-body interaction between the six water molecules, considered as one body, and the Cu^{++} as the other. On the right of Fig. VI,1 this analogue is pictured with the system at its equilibrium distance. As indicated earlier, this de-hydration interaction takes place in the volume interphase labelled Diffuse in Fig. V,1.

The potential energy versus distance curve will be calculated using the following data --
The equilibrium distance for water-ion system (r_e) is assumed equal to the radius of the hydrated Cu^{++} complex, and taken as equal to 0.5 nm as indicated by Reynolds and Lumry[55]. The free energy change of hydration for $CuSO_4 \cdot 12H_2O$ is assumed to be equal to the value of individual ions in infinite dilute solutions. As mentioned in section II,L,4 there are very few authors which report values for free energy change of individual ion hydration and these appear to fall in the range 490 ± 10 kcal (Hunt[175], Chernomorskii[99]). Since the critical evaluation of this data lies beyond the scope of this work, the value 490 kcal/g-ion will be used for Cu^{++} individual free energy change of hydration, which correspond to about 21.2 eV/ion. A value smaller than 490

will not alter the qualitative interpretation of our calculations, instead, will increase the value of the excess energy.

The expression for the Morse function[174] which is used for obtaining potential energy values as a function of separation distance is:

$$V = L\ \{1 - \exp)-\beta q)\}^2 \qquad \text{VI,1}$$

where:

V : potential energy (eV)

L : individual ion free energy of hydration (eV) and (cm^{-1})

β : Morse's constant (cm^{-1})

$$\beta = \tilde{\nu}\ \{2\pi^2 \mu c/(Lh)\}^{\frac{1}{2}} \qquad \text{VI,2}$$

where:

L : is expressed in cm^{-1}

$\tilde{\nu}$: wave number or characteristic vibrational frequency (cm^{-1})

μ : reduced mass, and for copper and six water molecules:

$$\mu = \frac{1.05\text{x}10^{-22} \text{ x } 6 \text{ x } 0.299\text{x}10^{-22}}{1.05\text{x}10^{-22} + (6 \text{ x } 0.299\text{x}10^{-22})} = 0.662\text{x}10^{-22} \quad \text{(g)}$$

h : Planck's constant

q : internal displacement = $(r-r_e)$ (cm)

r : separation distance (cm)

r_e : equilibrium distance (cm)

If the value of $\tilde{\nu}$ is taken as 500.0 cm^{-1} as indicated by Hush[172], the curve presented in Fig. VI,2 is obtained.

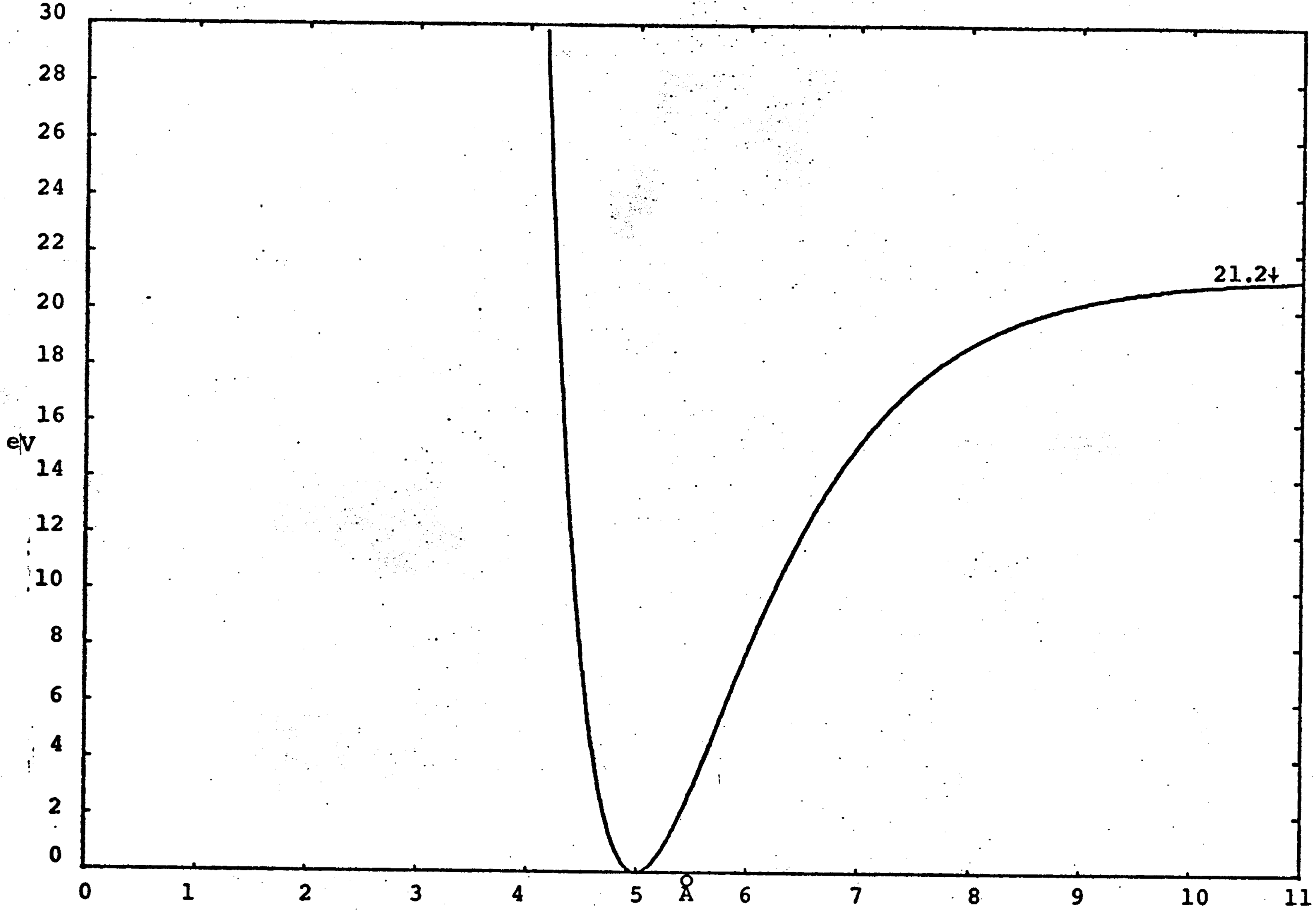


Fig. VI,2 - Potential energy function for hydration of copper divalent ions.

Basolo and Pearson[96] calculated values for what they call 'symmetrical breathing frequency' of 394 cm^{-1} for $Zn(H_2O)_6^{++}$ and 430 cm^{-1} for $Fe(H_2O)_6^{++}$, thus the above value for copper appears to be of the right order of magnitude. It is instructive to point out that the effect of the value of the characteristic frequency on the shape of the curve is such that, the lower the value of $\tilde{\nu}$ the more open is the well. Conversely for high values of $\tilde{\nu}$ the potential well is narrow with a sharp minimum, (this point is illustrated in Fig. VI,4 of the section which follows). If this latter curve is used for the calculation of the electrode layer thickness, very small values will result, as we have seen in reviewing Butler's work in section II,G,3.

C. DE-IONIZATION

1. Inherent Driving Force

As mentioned earlier, this attractive interaction, in the absence of externally applied potential energy difference, is the only inherent driving force for the metal deposition reaction.

The cuprous ion is not considered in this system; since it is experimentally easy to set conditions such that it will not be formed.

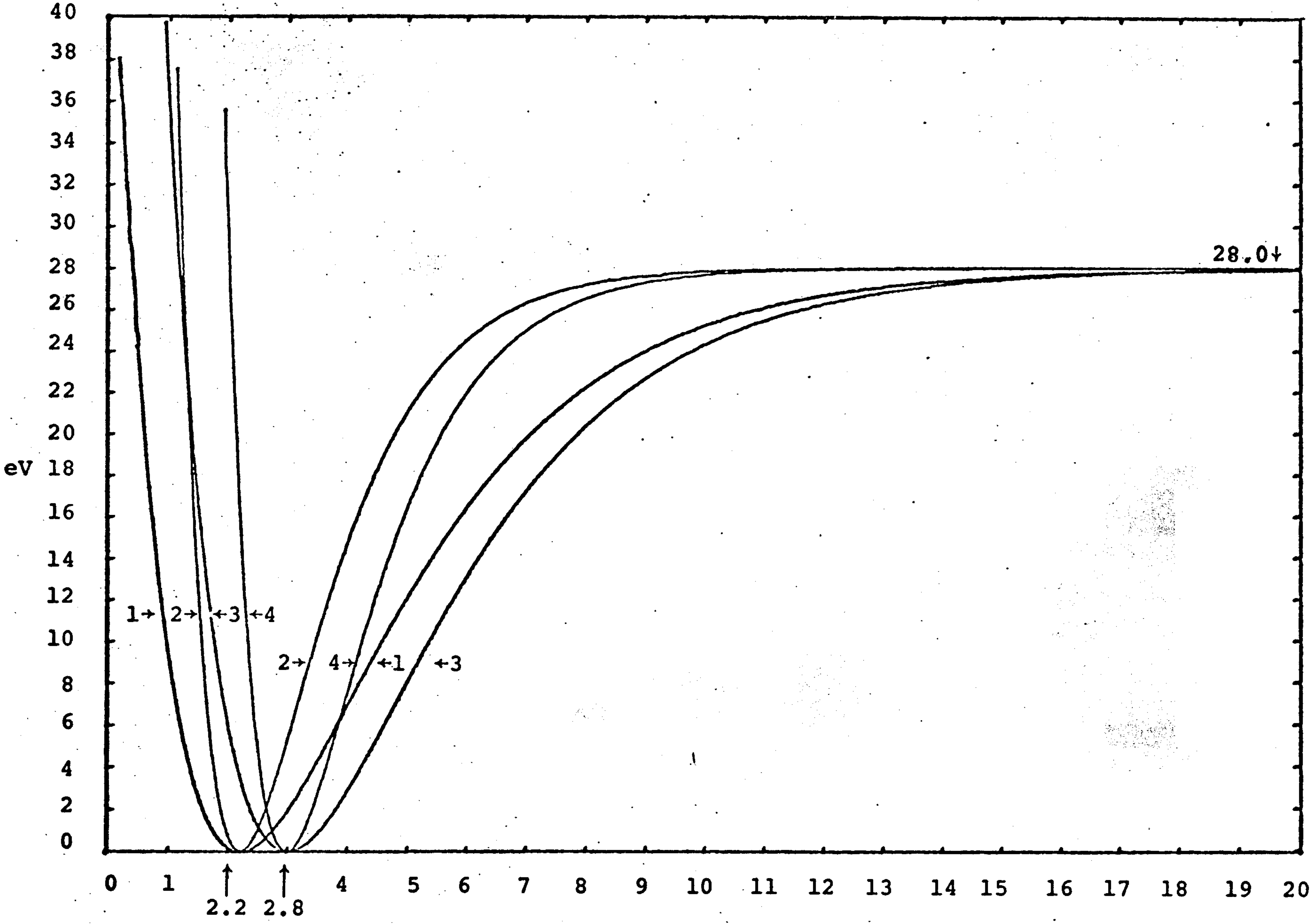


Fig. VI,4 - Potential energy functions for de-ionization of copper divalent

2. Ionization Potential Energy Function

Here again the Morse function will be used to describe the cupric ion/electron interaction in terms of the following analogue for the two-body interaction. The incoming Cu^{++} is taken as one body, while the two electrons and an atom at the first layer of the selvedge are considered the other body, as sketched in Fig. VI,3.

In order to determine the appropriate value for the equilibrium distance for this system, consider the following:

- the equilibrium internuclear distance for Cu_2 molecules is reported[110] as 2.2197 Å
- the diameter of a copper atom is 2.551 Å[110]
- the interparticular distance for molten copper in 1100°C is reported by Hosemann et al.[87] in 2.8 Å
- the diameter of Cu^{++} ion is estimated[96] as 1.44 Å.

Now, from discussion reported in the previous chapters of this thesis, a high value of the selvedge temperature is predicted; thus Hosemann's value should be used. However, very high values for the pressure are also predicted (see section II,M,3) which tend to reduce the equilibrium distance. Further, the newly formed atom at the selvedge surface may be considered also as forming a Cu_2 molecule with the surface atom.

Therefore, in order to show the effect of different equilibrium distances on the ionization potential energy function, Fig. VI,4 has been obtained where curves 1 and 2 are calculated using r_e = 2.2197 Å, while for curves 3 and 4

$r_e = 2.8$ Å is used. In addition, this figure also shows the effect of using different values for the characteristic vibrational frequency: curves 1 and 3 are obtained by using $\tilde{\nu} = 266.1\ \text{cm}^{-1}$ as indicated[110] for the Cu_2 molecule, and curve 2 and 4 using $\tilde{\nu} = 500.\ \text{cm}^{-1}$.

Values for the ionization potential of Cu^{++} published in the chemical literature 646 kcal/mol (Basolo and Pearson[96]) coincides with those of the physics literature 28.01 eV/ion (American Institute of Physics Handbook[110], 7.726 for the first ionization and 20.292 for the second). The reduced mass, μ, in this case is 5.225×10^{-23}g. The above values were then used in Eq. (VI,1) for the Morse function to obtain the curves in Fig. IV,4.

D. ELECTRON EXTRACTION ENERGY

The attractive interaction between electrons and the first layer of atoms of the metallic selvedge is assumed to be described by the Coulombic potential energy expression:

$$V = V_\infty - e^2/(4\pi\varepsilon r) \qquad \text{VI,3}$$

where:

V_∞ : total electron extraction energy (eV)

e : electron charge (C)

ε : dielectric constant in the interface ($C^2J^{-1}m^{-1}$)

r : separation distance (m)

Regarding the numerical value of the dielectric constant for the interphase between metal electrodes and aqueous electrolytic solutions, it does not seem that an expression for its precise calculation has been established as yet. From the literature survey we recall that Mott and Watts-Tobin[81] suggested a value for the dielectric coefficient <10, MacDonald and Barlow[109] 6, Bockris, Devanathan and Muller[83-84] 5.3, and Barradas and Sedlak[85] 4.6 -. From the characteristics of the electrolytic solution being considered, as indicated in section VI,B,1, we can predict that the contribution of the ions to the local field within the interphase will be large, thus the numerical value of the dielectric constant will be small. Therefore, Barradas's and Sedlak's value of 4.6 is selected as the one applicable, taking into account also the concentration (0.795 M) for which this value is reported.

As discussed in section V,6, the value of the electron extraction energy in electrode processes is also a matter of wide disagreement. However, the standard thermodynamic potential for the hydrated electron, as calculated by Kenney and Walker[112] in -2.7 eV, can be considered as the numerical value of the energy required to extract an electron from a metallic copper surface in contact with the aqueous electrolyte considered, under reversible conditions of equilibrium. Further, the value reported by Yurkov[114] for electrorefining of copper at high current density, -2.0 eV, can be taken to represent the value for the electron extraction energy under live dynamic process conditions.

By using Eq. VI,3 with the above indicated values for V and ε, and setting the zero at the equilibrium value of potential energy as described in section IV,4, the electron extraction energy function is obtained. In Fig. VI,5, curve (KW) for equilibrium conditions and curve (Y) for far from equilibrium conditions are reproduced.

It is worthwhile noting that when Kenney's and Walker's value of -2.7 eV is used (with Barradas' and Sedlak's $\varepsilon = 4.6$) the zero value of the potential energy corresponds to a distance of 1.159 Å. This value lies between one half of the internuclear distance for Cu_2 molecule (2.2197 Å), and the radius of the copper atom, 1.275 Å. This result seems to be consistent with the characteristics of the -2.7 eV which is a value for thermodynamic equilibrium. Moreover, the slope of the curve at 0.0 eV (equilibrium position) is 4.0 eV per Å corresponding to an electric field strength of $4 \times 10^{10} Vm^{-1}$. However, when the value reported by Yurkov for live dynamic electrorefining, -2.0 eV, is used (again with $\varepsilon = 4.6$) the zero potential energy corresponds to a distance of 1.564 Å which is comparable (but larger) with one half of Hosemann's et al.[87] interparticular distance, for molten copper at 1100°C, of 2.8 Å. This result seems to be

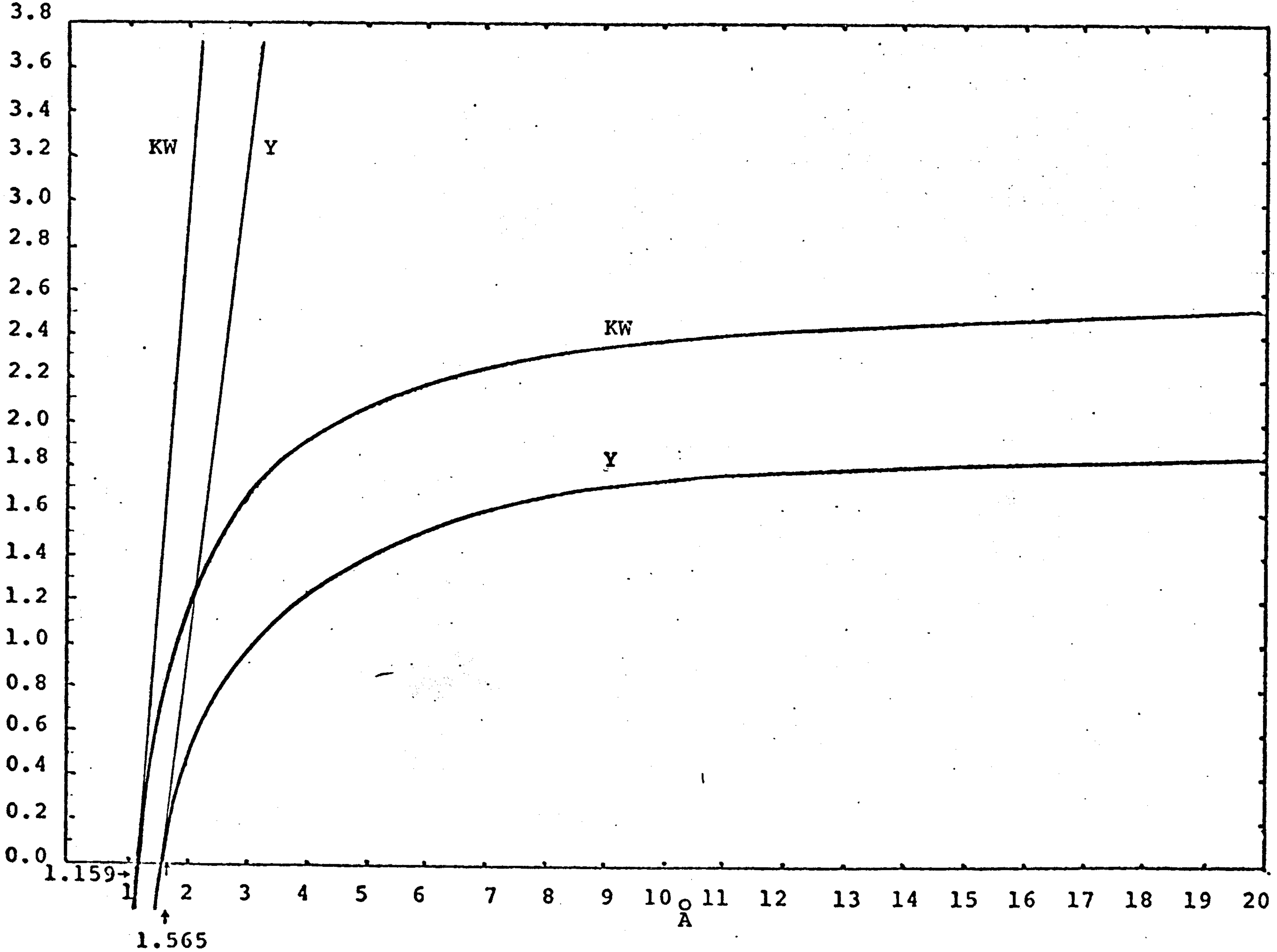


Fig. VI,5 - Potential energy functions for electron extraction energy; Curve KW: $V = 2.7$ eV. Curve Y: $V = 2.0$ eV. The electric in agreement with the features of live dynamic processes as discussed in terms of the electrodynamic model. Thus, under dynamic conditions the atoms at the selvedge have high energy values. Moreover, the slope of the curve at 0.0 eV appears to be 3.0 eV per Å, which corresponds to $3 \times 10^{10} \mathrm{Vm}^{-1}$. The fact that this value is smaller than that for equilibrium conditions may be attributed to the Thomson effect. For since the selvedge is at a higher temperature than the bulk metal, the electrons flowing against the temperature gradient gain potential energy (by absorbing energy), with the result that less additional energy is required in order to transfer electrons into the electrolyte.

E. GRAPHICAL INTERPRETATION

1. Introduction

At this stage we have enough data to proceed to the determination of the values for the variables associated with the cathodic copper reduction process, namely: the location of the Wien plane, of the electronation point, the energy the newly formed atom has at the electronation point, and the amount of excess energy. This can be accomplished graphically by superimposing the curves representing the description of the various species interactions as calculated in the previous sections.

In Fig. VI,6, Fig. VI,2 and Fig. VI,4, are reproduced, on the same scale, superimposed in such a way that the cupric ion at the point (A) can be considered as being located at infinite distance both from the six water molecules and from the selvedge. Therefore, the potential energy value for the Cu^{++} in position (A) is the same whether we consider the de-ionization interaction or the hydration interaction, since this ion is in an unstable equilibrium position, in which it has the same tendency of being attracted both by the electrode and by the molecules of water. It is apparent from the above observations that the coupling of the two curves in the way in which it is represented in Fig. VI,6 is correct.

Now, we induce the cupric ion to undergo hydration; thus it moves to position (B), which corresponds to a hydrated complex with the geometrical configuration sketched in Fig. VI,1 (on the left side). We can see that in moving from position (A) to (B) the ion-water molecules system has lost approximately 21. eV of potential energy which is converted into energy. This energy is the free energy of hydration which is transferred to neighboring 'free' water molecules in order for the new hydrated ionic complex to stabilize close to the equilibrium position (B).

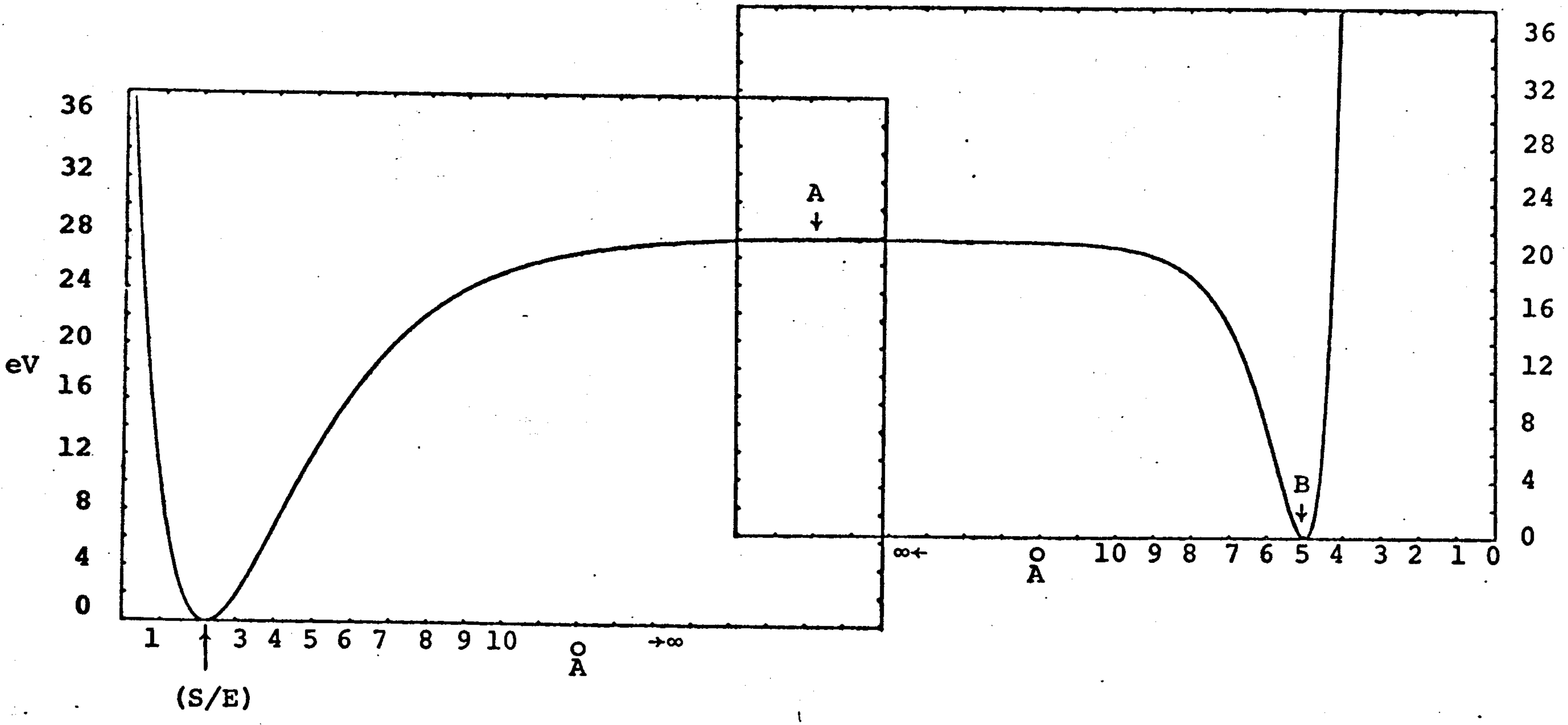


Fig. VI,6 - Superimposition, on the same scale, of the curves reproduced in Fig. VI,2 and Fig. VI,4.

2. Cathodic Deposition Without Overpotential

On the basis of the reasoning presented in the introduction, consider the copper ion hydrated complex in the solution bulk (SB)* being brought (by processes other than difference in electric potential) at the plane (D/B). This new situation is illustrated schematically in Fig. VI,7 in which the semi-infinite dimension of position (A) of Fig. VI,6 has become a location of a balance between two two-body systems which are in competition for one common body; this location is the Wien plane, as described in section V,10.

At this point it is important to note that what Fig. VI,7 depicts, is actually the classical potential energy-distance profile of Fig. I,1, but with all its characteristics explained and numerically evaluated. Let us describe them as given in Fig. VI,7:

The process of electronation of a cupric ion involves its transfer across a distance of approximately 21. Å, from position (D/B) in hydrated form, to position (S/E) corresponding to the electrode first atomic layer. The values of potential energy the ion acquires first with the hydration and then with the de-ionization interaction are given, for all points between (D/B) and (S/E), on the overall curve.

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* This terminology refers to Fig. V,1.

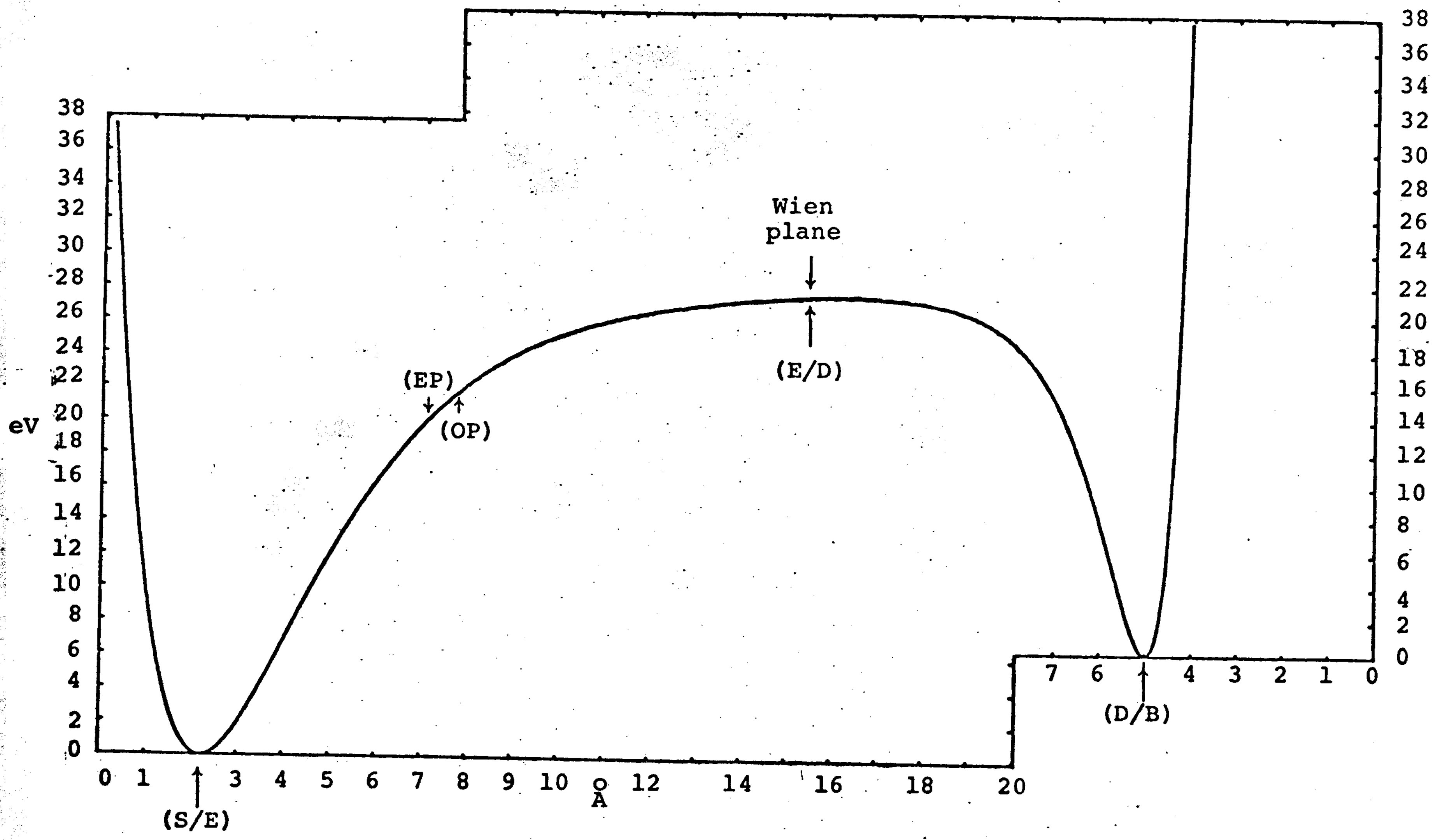

Fig. VI,7 - Potential energy-distance profile for copper divalent electronation reaction.

However, we are concerned with energy the ion atom has at any point along the (D/B) - (S/E) path. Therefore, conversely to the hydration process described earlier, to go from position (D/B) to position (E/D) the ion water system must absorb 21. eV of energy from the surroundings and store it in the form of potential energy. The attractive force (the slope of the curve) first decreases slowly, then rapidly to a small value at (E/D). At this point the linear field strength between the ion and the water molecules at this particular separation distance is approximately over $3x10^{10}V\ m^{-1}$.

This part of the process is generally called 'activation' and it was discussed in previous chapters in terms of solvent fluctuation, symmetrical breathing, and excess energy in connection with the exchange current. Further, it is interesting to calculate the magnitude of the linear velocity of the ion during the vibrational motion relative to the water molecules of hydration, at the equilibrium point under active condition. This can be defined in terms of the Wien effect, as reported in section II,M,2 , and for which this linear velocity can be estimated as follows:

- the various values for water relaxation time, as compiled by Horne[92] for temperatures above 40°C fall into the order of magnitude of 10^{-12}s;
- the radius of the ionic atmosphere measured in Fig. VI,7 from (D/B) to (E/D) is 7. Å;

thus, the ionic linear velocity is 700. m s^{-1} which corresponds to a kinetic energy of the copper ion relative to the water molecules, of 0.16 eV. Interestingly, one can deduce from this value that only a minor part of the system energy is associated with its internal vibration.

The ion at the Wien plane now starts becoming influenced by the de-ionization attraction, and at this point the linear field strength between the ion and the electrons on the selvedge is approximately $2x10^{10}$V m^{-1}. It is worthwhile noting that these field strength values are of the order of magnitude (10^{10}V m^{-1}) predicted by various authors as reviewed in the literature survey. Consequently, the liberated ion moves from (E/D) toward (S/E) because of the increasing de-ionization attractive interaction. This approaching motion results in an increase in the electric field strength magnitude between the ion and the electrons at (S/E), up to a point in which it becomes larger than the strength of the electron extraction interaction, which was indicated in Fig. VI,5 as $2x10^{10}$V m^{-1}. This location is the ion electronation point (EP) and two electrons will therefore be transferred to the ion from (S/E) with an energy expenditure of 2. eV per electron (or 2.u eV, if near equilibrium is assumed).

In summary, the newly formed atom at (EP) has a residual potential energy, with respect to the selvedge equilibrium value of approximately 16. eV (20 minus 4) which is associated with a kinetic energy obtained from the transformation of 8 eV of potential energy. The linear velocity of the new atom at that point can be estimated in a manner similar to that which was used before at approximately 5,000. m s^{-1}.

At this moment, the second time period of the electrode process begins. The amount of kinetic energy will be sufficient, under the considered conditions, to transfer the newly formed atom to the selvedge. In addition, as indicated earlier, some water repulsion and the de-atomization energy will be available at short distances from (S/E) due to short range forces. As for an order of magnitude of the de-atomization energy we can assume the dissociation energy of the Cu_2 molecules (1.97 eV)[110] as being a representative order of magnitude.

The conclusion which may be drawn from this analysis for the case of no overpotential is that the newly formed atom reaches the selvedge with approximately 16. eV of excess energy.

3. Cathodic Deposition With Overpotential

The effect of applying a low overpotential (0.05 V for example), as has been qualitatively indicated in the previous chapters, is to shift the location of the electron surface toward the electrolyte side of the interphase. By considering Fig. VI,5, we see that for an increase in distance from the equilibrium position (corresponding to 0.0 eV) the slope of the potential energy-distance curve for the electron extraction system decreases. Therefore, in Fig. VI,7, the field strength necessary to transfer the electrons is achieved by the ion at an earlier location. This results in the occurrence of the electronation further away from the selvedge (for illustration, point (OP) in Fig. VI,7).

In analogy with the treatment used in the previous section, we can see that the newly formed atom has a higher value of potential energy and it is associated with a lower value of kinetic energy than for the previous case without overpotential. However, other operating conditions being the same, the water repulsion can be thought of as being more effective in driving the atom towards the electrode than in the case dealt with in the previous section. Therefore, the amount of excess energy the newly formed atom has to transfer to the electrode can be assumed as approximately the same as under near equilibrium conditions.

In the case of high overpotential (0.5 V for example) the electronation point is further away from the electrode, up to the point, upon further increase in overpotential, in which the newly formed atom will not be able to reach the selvedge, thus resulting in the formation of powdery deposit.

By extending this line of reasoning, it can be seen that for overpotential larger than 2.V, in the case of copper deposition, the electrons will be freed from the interaction with the selvedge, and will thus be injected into the electrolyte where they will become hydrated and subsequently may produce colloidal metal fog at large distances from the electrode as reported by Kenney and Walker[112].

4. Energy Flux, Energy Density and Temperature

The final numerical evaluation, on the bases of graphically obtained data, involves the estimation of the energy flux which crosses the (S/E) plane being transferred into the metal bulk.

Consider an overpotential of 0.5 V generating a current density of 50 mA cm^{-2}, with an excess energy of 16 eV/atom; the flux of energy is:

$$\frac{0.05(\mathrm{Cs^{-1}cm^{-2}}) \times 1.6\mathrm{x}10^{-19}(\mathrm{J/eV}) \times 16.\ \mathrm{eV}}{1.6\mathrm{x}10^{-19}(\mathrm{C/e^{-}}) \times 2(\mathrm{e^{-}})} = 0.4\ \mathrm{J\ s^{-1}cm^{-2}}$$

Finally, using the Georgian scale (see section II,O,2) let us attempt the estimation of the temperature of the newly formed selvedge, when the electrode process indicated in the previous sections has occurred for one second, with the hypothetical condition that no energy can be transferred into the metal bulk. From the previous estimate, we have a release of 0.4 J cm^{-2}, and the total amount of metal deposited on this area during one second is:

$$0.05(\text{C})/[2(\text{equiv}) \times 96{,}487(\text{C equiv}^{-1}\text{mol}^{-1})] =$$
$$= 2.59\text{x}10^{-7}\text{mol}$$

corresponding to an energy released per mole of metal:

$$0.4(\text{J})/2.59\text{x}10^{-7}\text{mol} = 1.544\text{x}10^{6}\ \text{J mol}^{-1}\ .$$

Converting into degrees K:

$$1.544\text{x}10^{6}/8.31434 = 1.85678\text{x}10^{5}\ ^{\circ}\text{K}$$

The significance of this last result cannot be overstressed, and shows the importance that the heat conduction characteristics of the substrate have on the selvedge temperature.

F. GLOBAL THERMODYNAMICS CALCULATIONS

1. Introduction

At this point it is appropriate to compare the values resulting from the global analysis for the whole copper electrorefining overall reaction in terms of global thermodynamics. This will give an insight into the relative magnitudes of, what have been called, 'promotional' and 'de-excitation' energies, and of the overall energy difference between initial and final state. Further, by difference, the value of the anodic cooling can be directly calculated.

2. Calculation of Entropy Internal Production

The energy balance in chemical thermodynamics is based on the following definitions:

Internal Energy: $E \equiv H - PV$ and $dE = dH - PdV - VdP$ VI,4

where:

H : the enthalpy

P&V : the pressure and volume;

Gibbs Free Energy: $G \equiv H - TS$ and $dG = dH - TdS - SdT$ VI,5

where:

S : the entropy

T : the temperature.

For reversible processes the general definition of free energy change:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} dn_i + \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n_i} dn_j + \left(\frac{\partial G}{\partial C}\right)_{T,P,n} dC + \left(\frac{\partial G}{\partial A}\right)_{T,P.n} dA \qquad \text{VI,6}$$

where:

C : Coulomb of charge

A : area, unit surface,

n_i : number of species i present

and the differential expression for reversible processes is:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i + \varepsilon dC - \gamma dA \qquad \text{VI,7}$$

where:

μ_i : the chemical potential of component i (species)

ε : the external potential applied

γ : the surface tension

Now, by substituting Eq. VI,7 into Eq. VI,2, and this result in turn into Eq. VI,4 we obtain:

$$dE = TdS - PdV + \Sigma \mu_i dn_i + \varepsilon dC - \gamma dA \qquad \text{VI,8}$$

where the term TdS, is the reversible energy contribution, also called the external contribution due to entropy exchange, termed Td_eS.

Thus, for reversible processes $TdS = Td_eS$. Now, the second law of thermodynamics states that for thermodynamically permissible processes $TdS \geq Td_eS$. Consequently, an irreversible process is defined for conditions in which

$$TdS - Td_eS = Td_iS > 0 \qquad \text{VI,9}$$

This quantity is the so-called Clausius uncompensated heat, corresponding to entropy internal production due to the irreversible nature of the process.

As discussed in section IV,9, surface tension, adabsorption and like phenomena are considered of minor importance in this study, therefore, the term γdA, in Eq. VI,8 will be neglected.

In order to observe the principle of the integrity of the electrochemical potential, the two terms representing the changes in chemical and electrical energy are unified as:

$$\Sigma\mu_i dn_i + \varepsilon dC = \eta dC \qquad \text{VI,10}$$

where η, is the difference in electrochemical potential energy of the species between the final and the initial state, defined as:

$$\eta = \{\tilde{\mu}_{i\,(\text{cathode})} - \tilde{\mu}_{i\,(\text{anode})}\} \qquad \text{VI,11}$$

where $\tilde{\mu}_i$ is the electrochemical potential energy of species i.

In summary, the combined statement of the first and second law for the energy balance of a reversible process is:

$$dE = Td_eS - PdV + \eta dC \qquad \text{VI,12}$$

while for an irreversible process:

$$dE = TdS - PdV + \eta dC - Td_iS \qquad \text{VI,13}$$

It is important to notice that η, as stated, is the difference between the value of electrochemical potential energy at the cathode (the final state of low potential energy) and the value at the anode (the initial state of high potential energy), thus is expresses a decrease in potential energy and therefore its numerical value has a negative sign indicating a decrease in internal energy. It follows that this decrease in potential energy corresponds to a release of energy, as discussed in section IV,4. Eq. VI,13 can be used to calculate this energy, the simplest case being an electrorefining process for which the overall reaction reduces to:

$$Cu^\circ_{(anode)} \rightarrow Cu^\circ_{(cathode)}$$

and thus dE=0. Since PdV can be considered negligible, we obtain also TdS = 0. Eq. VI,13 is therefore reduced to:

$$\eta dC = Td_iS \qquad \text{VI,14}$$

This expression is used to calculate the actual amount of heat irreversibly evolved, where η is expressing the amount of energy (a positive quantity) released by the decrease in potential energy of the system for one equivalent.

The rate at which this heat is generated is consequently obtained by using:

$$\eta I = Td_iS \qquad \text{VI,15}$$

where:

I : the current density in A m^{-2}

η : is in eV

consequently the rate is expressed in J $s^{-1}m^{-2}$.

The case of metal electrowinning follows in analogy, when the term Td_eS has been numerically evaluated as follows. The reversible heat generated or absorbed, corresponding to $T\Delta S$ for the reaction carried at the thermodynamic standard reversible potential defined as $\Delta G° = nFE°$, for any given density I, is:

$$Td_eS = \frac{T\Delta S\ I}{n\ F} \qquad \text{VI,16}$$

expressed in J $s^{-1}m^{-2}$.

A numerical evaluation of the quantities discussed in this chapter will now be attempted. Using Eq. VI,15, the rate of irreversible heat generation can be calculated under the previously indicated conditions of overpotential (0.5 V) and current density (50. mA cm^{-2}):

$$\frac{\eta I}{n} = \frac{0.5(V) \times 0.05(Cs^{-1}cm^{-2}}{2(\text{equiv})} = 0.0125\ J\ s^{-1}cm^{-2}$$

Recalling the result obtained in section VI,E,4 for the cathodic excess energy (0.4 J $s^{-1}cm^{-2}$) we can see that the difference between these type of values is over an order of magnitude.

And, finally, since the global thermodynamics gives overall values for the energy changes, as discussed in section we can, by subtraction, determine the numerical value of the anodic cooling effect:

$$0.0125 - 0.4 = -0.3875 \quad J\ s^{-1}cm^{-2}$$

In copper electrowinning systems instead, since at the anode reactions different from the copper dissolution take place, namely oxygen de-electronation and evolution, $T\Delta S \neq 0$. Therefore, the calculation of the anode energy change must be performed taking into account these reactions also. However, because of the complexity of this anodic system, which was discussed in the literature survey (section II,Q,3) and since it was not the prime intention of this investigation, its analysis has not been performed.

CHAPTER VII. EXPERIMENTAL INVESTIGATION

A. INTRODUCTION

1. Selection of the Appropriate Experimental Approach

The direct measurement of the intrinsic quantities involved in the electrodynamic model is considered as the appropriate experimental approach in order to verify the correctness of the analytical development. Therefore, for the case of cathodic excess energy and anodic cooling, an experimental system which will permit the direct measurement of the changes in the electrode surface energy during the progress of the reaction must be used.

The methods available for investigating electrode/ electrolyte boundary layers during metal electrochemical processes for which most of the published work has been carried out, have been reviewed by Brenner[175]. They can be divided into three classes which are given below with their limitations --

a) optical methods - are not suited to the analysis of inorganic complex systems at current densities at which gas evolution occurs;

b) sampling methods - single capillary and microporous electrode disturb the equilibrium when the interfacial electrolyte layer is drown off and the composition averaged;

c) freezing technique - rapidity of freezing and microsectioning instruments are the limitations.

An experimental method which will allow the determination of the distribution in energy in the electrolyte/electrode interphase and thus provide detailed understanding of its structure, species chemical identity and rate of reaction, under dynamic, live process conditions, is still to be developed.

To the author's knowledge, nearly all the investigations of the electrode process have been attempted from the solution side of the electrode/electrolyte interphase; semitransparent thin electrodes, and electrode change in resistivity being the only exceptions. Since the aim of this experimental investigation was to obtain information on the energy changes occurring at the electrode/electrolyte interphase, and the author being a metallurgist, the interphase was approached from the metal side. Using thermoelectric elements as electrodes, the generated thermoelectric phenomena were monitored.

2. Considerations on the Application of a Thermoelectric Element as the Test Electrode

The first criterion in the selection of the thermoelectric couple to be used as the test electrode was the compatibility with the electrochemical variables as indicated in the previous chapter; primarily with regard to concentrated metal sulphate acid solutions, and cathodic and anodic overpotentials.

Moreover, in view of the small magnitude of the heat generated, which was calculated in the previous chapter to be in the range of 1. W cm^{-2}, the second criterion was in regard to the magnitude of the temperature coefficient of the couples considered; the largest $(\partial E/\partial T)$ being sought for the best resolution of the small temperature change expected.

Consequently, Copper-Constantan (55Cu,45Ni) was the natural choice for the copper electrorefining system. A 0.5 mm diameter Constantan wire was welded at the center of a copper foil. The use of this assembly as the test electrode in a copper electrorefining cell with potentiometric recorder binding posts being the reference junction resulted in readings in the millivolt range which were linear function of the cell current. This result occurred because the largest contribution to the reading was the voltage drop across the copper foil from the copper current lead (where also the copper branch of the thermoelectric device was connected), to the point of the welded Constantan wire. Therefore, the voltage drop was proportional to the cell current.

In order to reduce the non-thermoelectric potential difference across the electrode surface, thus its contribution to the total microvolt reading, a copper-Constantan thermocouple bead, (obtained by welding two 0.5 mm diameter wires) was used as the test electrode with an immersed surface of approximately 6. mm^2. When the copper branch of the thermocouple was also used as the current lead, under cathodic mode (high electron activity) the microvolt potentiometric reading decreased with increasing cell current; whereas, under anodic mode (low electron activity) the reading increased. The opposite behavior occurred when the Constantan branch of the thermocouple was used as the current lead. This phenomenon was attributed to the large difference in resistivity between the two legs of the thermocouple (copper 1.56 μΩ cm vs.[110] Constantan 48.9 μΩ cm).

In order to reduce the voltage drop through the thermoelectric circuit, a third wire was used as the current conductor to the thermocouple bead. A three wire thermoelectrode (from here on it will be written TE) was constructed by arc welding two copper and one Constantan 0.5 mm diameter wires, to form a bead of 2 mm in diameter. Ceramic insulators and a glass tube with silicone adhesive tightly masked the electrode down to the bead, to leave 5 mm^2 as the test electrode immersed surface. The current lead was connected to one of the copper wires thereby leaving the other copper wire as the positive terminal of the thermocouple and the constantan as the negative, which were then connected to the appropriate terminals of the potentiometric recorder. Tests resulted in readings analogous to the previous assembly. However, the microvolt-current relationship had a much lower slope than before.

To further reduce the voltage drop contribution to the total voltage reading of the potentiometer, thermoelectric elements of wire which were closer in the value of their resistivity were used. A three wire TE was constructed by arc welding two platinum wires (resistivity at 0°C, 9.83 μΩ cm) with one Pt-13%Rh wire (19.0 μΩ cm) of 0.5 mm diameter. The current was supplied to the bead through a platinum wire, while the other Pt wire was connected to the negative terminal of the recorder; the Pt-13%Rh branch being connected to the positive terminal. Readings with the same characteristics as previously reported (anodic increase and cathodic decrease) were obtained, but the microvolt-current relationship had a much lower slope than in the last copper-constantan system.

For a clearer insight of the effect of the voltage drop on the total microvolt reading, a three wire electrode without thermoelectric effect generation capability was used.

An all copper system electrode was constructed by welding three copper wires into a bead; connecting one to the current lead and the other two to the terminals of the recorder. Current up to 0.9 A was supplied under cathodic mode and corresponding voltage of up to 1.05 V. This resulted in a decrease in microvolt reading, while the magnitude of the decrease was proportional to the total cell current. The opposite phenomenon was observed up to 0.5 A and 3.0 V in anodic mode, confirming the characteristic behavior observed in all the previous instances. Thus, the two wires connected to the potentiometric recorder measure a potential difference across the points at which it is connected to the bead, since in order to make electrons flow through it a voltage difference is required. From here on this effect will be referred to as "solid state effect" and written SS.

Since the output of the thermoelectric effect should not be a function of the junction dimensions, then, to reduce the contribution of the SS effect (which is a function of the bead dimensions) to the total reading, the use of a small bead would then allow a better resolution of the electrochemical contribution to the total microvolt reading. Therefore, in order to investigate the effect of the bead geometrical dimensions on the total microvolt output, two three-wire TEs, made of Pt-Pt13%Rh-Pt, were arc welded to form two differently shaped, approximately spherical beads: TE#1 of 1.6 mm in diameter, and TE#2 of 0.5 mm in diameter.

Under identical electrochemical conditions as for the previous tests, the results for TE#1 were as before -- cathodic decrease and anodic increase in the microvolt output. However, much larger signals were obtained from TE#2 (the small bead) and also their dynamic behavior was different. For the small bead under cathodic mode there was an initial instantaneous decrease followed by an increase past the neutral position. This effect was not present in the case of the larger bead. These results proved that because of the larger surface to volume ratio of the small bead, the surface bound electrochemical effect now appeared; conversely, the volume bound SS effect was comparatively dwarfed.

The effect of the wire configuration was now studied (since the three wires were not in perfectly symmetrical positions with respect to each other and the center of the bead) by interchanging the platinum wire, which was the current lead in the previous test of TE#2 (the small bead) with the Pt wire which previously was the thermoelement. Everything else was kept the same as before, and on running again, the initial instantaneous cathodic decrease disappeared. It was therefore clear that in order to use thermoelectric devices as electrodes, a baseline for each particular TE is required. Basically, a curve of cell current versus microvolt output which contains the contribution of the SS effect occurring for the particular configuration. The departure from the datum baseline is then due solely to the thermoelectric effects. However, in order to obtain such a calibration of the TEs, a fourth wire is needed to carry the electrons in or out of the bead in a similar way to which occurs during the electrode process.

In conclusion, these preliminary considerations on the application of thermoelectric elements as test electrodes showed that the characteristics of a successful thermoelectrode (TE) for the measurement of the values of cathodic excess energy and anodic cooling are primarily the following:

- the smallest practical dimensions, since the thermoelectric effects are not a function of the dimensions of the junction, whereas the parasitic ohmic (SS) effect is a function of dimensions. Therefore, the maximum surface to volume ratio must be sought;

- a symmetrical configuration of the wires and the bead should be achieved, or a datum baseline for the SS effect must be obtained for each TE using the fourth wire.

3. Speculations on the Interpretation of the Thermoelectrode Output

The results of the monitoring of electrode reactions, when obtained in a graphical form from a potentiometric strip chart recorder, will be called 'thermoelectrogram'. These will show a series of peaks, plateaus, and valleys corresponding to the energetics of the reactions occurring at the particular time.

If we are to speculate on the correlations of these results with the type of morphology of the deposit, we can make the following general considerations on a relative basis: A small positive reading will indicate that the metal being deposited will produce, under those conditions, a small value of excess energy. Therefore, the morphology of the deposit will be expected to be flat and smooth, since, as will be discussed in section VII,D,5, these are not conditions to produce a dendritic deposit. A large positive output, instead, will indicate that the metal deposit is not to be expected to be smooth, on the contrary, whiskers and powder will generally result.

It must be stressed however, that the presence of side reactions, simultaneously occurring at the electrode, might alter the magnitude of these readings. Therefore, the above general guidelines are applicable only to systems which fulfill the assumptions made in the development of the numerical analysis in section VI.

B. THE THERMOELECTRODES AND INSTRUMENTATION

1. Introduction

Two types of apparatus were used in this experimental investigation which can be divided into two categories of tests:

1) thermoelectrodes made from 250 μm diameter wires of platinum and Pt-13%Rh, which will be referred to as 'large TE', for experiments at high current density (>100. mA cm^{-2}) with agitated electrolyte;

2) thermoelectrodes made from 25 μm diameter wires of platinum and Pt-13%Rh, which will be referred to as 'small TE', for experiments at low current density (<100. mA cm^{-2}) without agitation.

This division of the experimental tests is appropriate in describing the sequence of the development of the thermoelectrode. The first series of experiments showed that the approach was promising, although the results were still affected by parasitic SS effects, and indicated the modifications required in order to obtain the best measurements of the electrodynamic variables. The second series of experiments was performed with the best experimental technique available at the present stage of development, and produced results representing the effect of the electrode reaction only.

2. Large Thermoelectrodes at High Current Density with Forced Flow

The apparatus used for this series of experiments was arranged as sketched in Fig. VII,1, where the power supply (8) Hewlett Packard 6263B, constant current 0-10 Amp constant voltage 0-20 volt, is connected with the cylindrical counter-electrode (6) (from here on written CE) made of the same metal as the one being tested, and through a shunt ammeter (9), to the wire (1) of the four wire TE (5). TE and CE are immersed in the electrolyte contained in transparent plexiglass rectangular vat (7) with dimensions 11.5 x 11.5 x 10. cm. To allow the free circulation of the electrolyte upward through the CE into the TE, the upper edge of the cylinder was maintained 1. mm below the electrolyte surface. A digital voltmeter (10) Hewlett Packard 3430 is used to measure the potential difference between CE and TE. One pen of a Honeywell 194 potentiometric ($10^4 \Omega/mV$) strip chart recorder (12) measures the electromotive force generated by the TC formed by wires (2) and (3) which are part of the TE. The thermoelectric junction at the reference temperature (14) electrically isolated is placed underneath the CE in proximity of the upward directed electrolyte flow. The voltage across the shunt, which is used for current monitoring is recorded on the other pen of the recorder. The pump (13) provides the forced electrolyte flow.

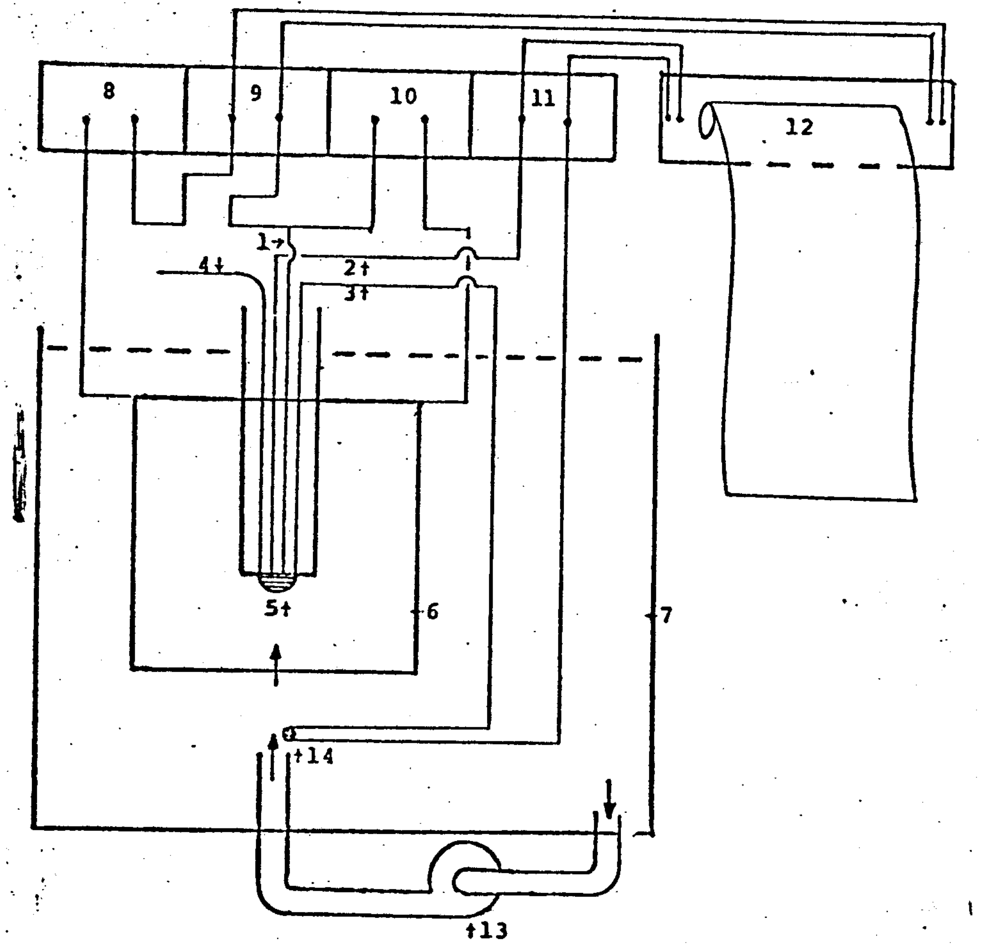

Fig. VII,1 - Schematic representation of the apparatus used for the large TE series of experiments. (The

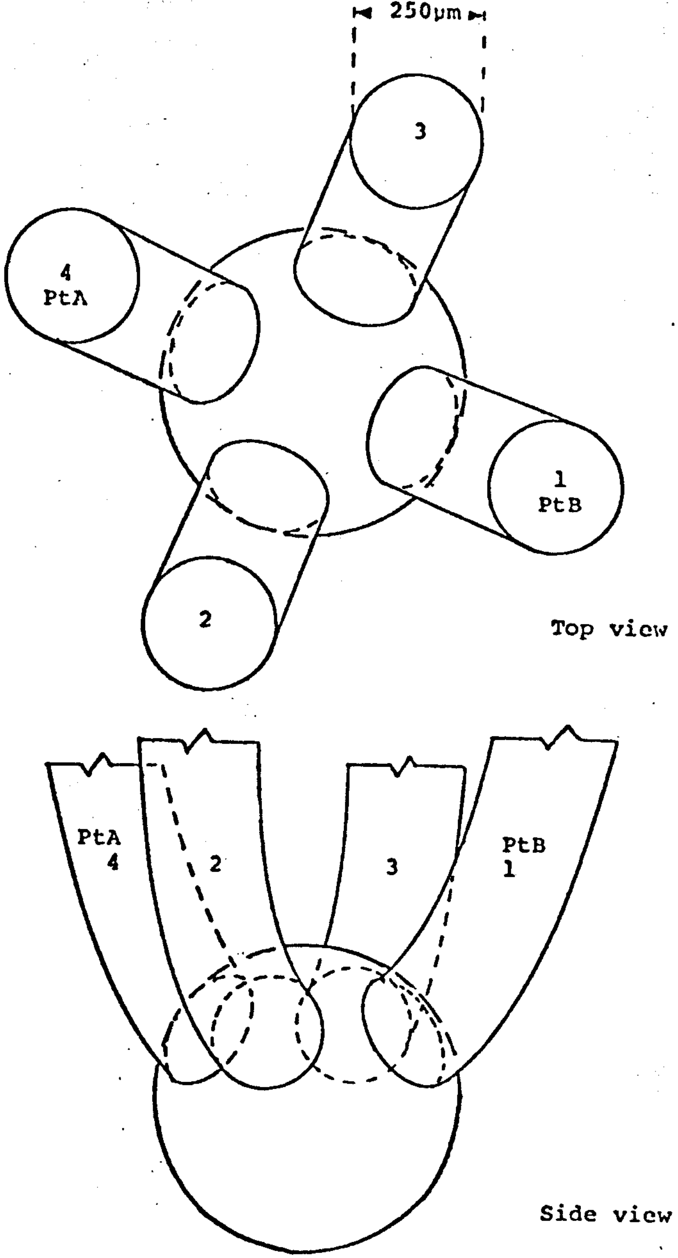

Fig. VII,2 - Ideal geometrical configuration for

Fig. VII,2 shows the ideal geometrical configuration of Tes which were constructed by arc welding three platinum and one PT-13%Rh wires, 250. μm in diameter, together to form a bead of approximately 1,000. μm in diameter. The wires inserted through a four hole ceramic isolator, made electrolyte tight with silicone rubber (Dow Corning glass and ceramic adhesive) which masked also part of the bead, leaving uncovered only its lower hemisphere (opposite to the termination of the wires); this surface of about 10. mm^2 being the test electrode.

A periodic reversed polarity dry calibration was performed for each TE using wires #1 and #4 (PtA and PtB in Fig. VII,2). The amplitude of the peak to peak voltage difference between the forward and reverse currents was recorded. The TEs which had a value higher than 10.μV per 100.mA of total current (corresponding to 3.18 A cm^{-2} at the bead cross section) were discarded. This value of 10.μV was set as representing the maximum allowable asymmetry in the bead configuration, since a reference electrode with the particularly bad asymmetry reproduced in Fig. VII,3, composed of four identical 250.μm diameter platinum wires (no Pt-13%Rh), resulted in 2.5 μV per 100. mA flowing through leads Pt3 and Pt7, when leads Pt2 and Pt4 were connected to the potentiometric recorder terminals.

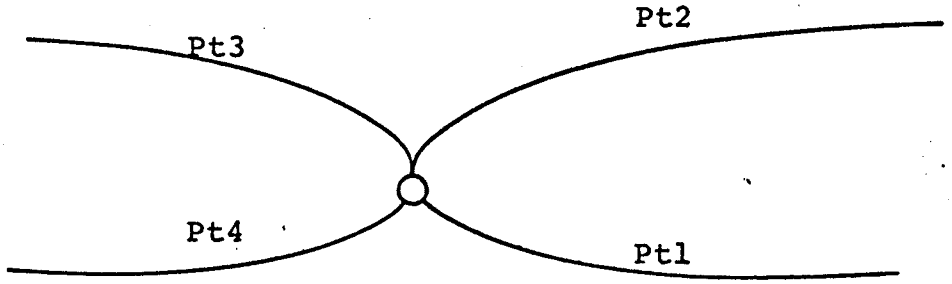

Fig. VII,3 - Electrode reference for asymmetry.

This all platinum electrode, incidentally, was tested as an electrode in copper system with Pt1 as the current lead and Pt3 isolated. Microvolt output resulting from Pt2 and Pt4 was nearly identical to the previous dry calibration test.

In addition, this provided experimental confirmation that the contribution of the Joule heating effect for the apparatus described can be considered negligible (as calculated in the discussion section of this chapter, since the magnitude of the forward peak was nearly equal to the reverse peak which had opposite sign.

It is important to reiterate that the SS effect in cathodic mode generates a decrease in microvolt reading, while in anodic mode an increase results.

3. Small Thermoelectrodes at Low Current Density in Quiescent Electrolyte

The apparatus used in this series of experiments was an improved version of that previously described for large TE; Fig. VII,4 shows the whole instrumentation under operating conditions, and Fig. VII,4,b its circuit diagram.

The current source was a Keithley 225, a precision constant current supply between 10^{-9} and 10^{-1} A, up to 100. v. The potential difference between thermoelectrode and counterelectrode was measured by one of the pens of one of the Honeywell 194 strip chart recorders. The other pen of this recorder registered the emf generated by the TEs. The second Honeywell 194 recorded the voltage analog output of a Keithley 610C electrometer measuring the current with one pen and the electrolyte temperature with the other.

A 267 ml Hull cell was used as the electrolytic bath, thus the counterelectrodes were metal anodes as commercially available and supplied by R.O. Hull Co.

The reference junction for the thermoelectric circuit was placed right next to the TE test surface as shown in Fig. VII,6 which represents the ideal configuration of the TEs used in this series of experiments. However, the best achievable configuration is shown in Fig. VII,7, in which the TE is photographed without the electrical isolator to allow for the observation of the geometry and dimensions of

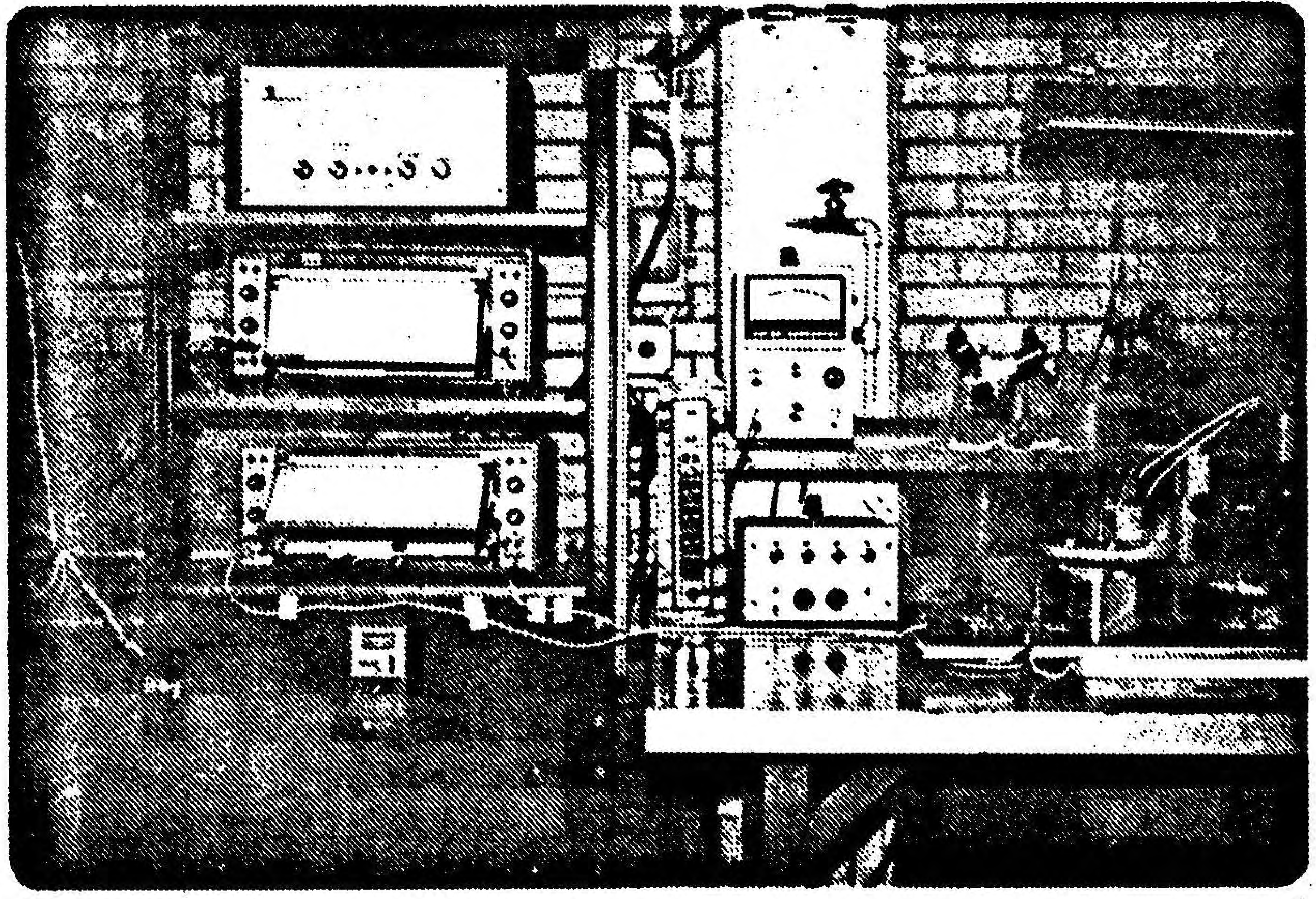

Fig. VII,4 - Apparatus used in the small thermoelectrode series of experiments.

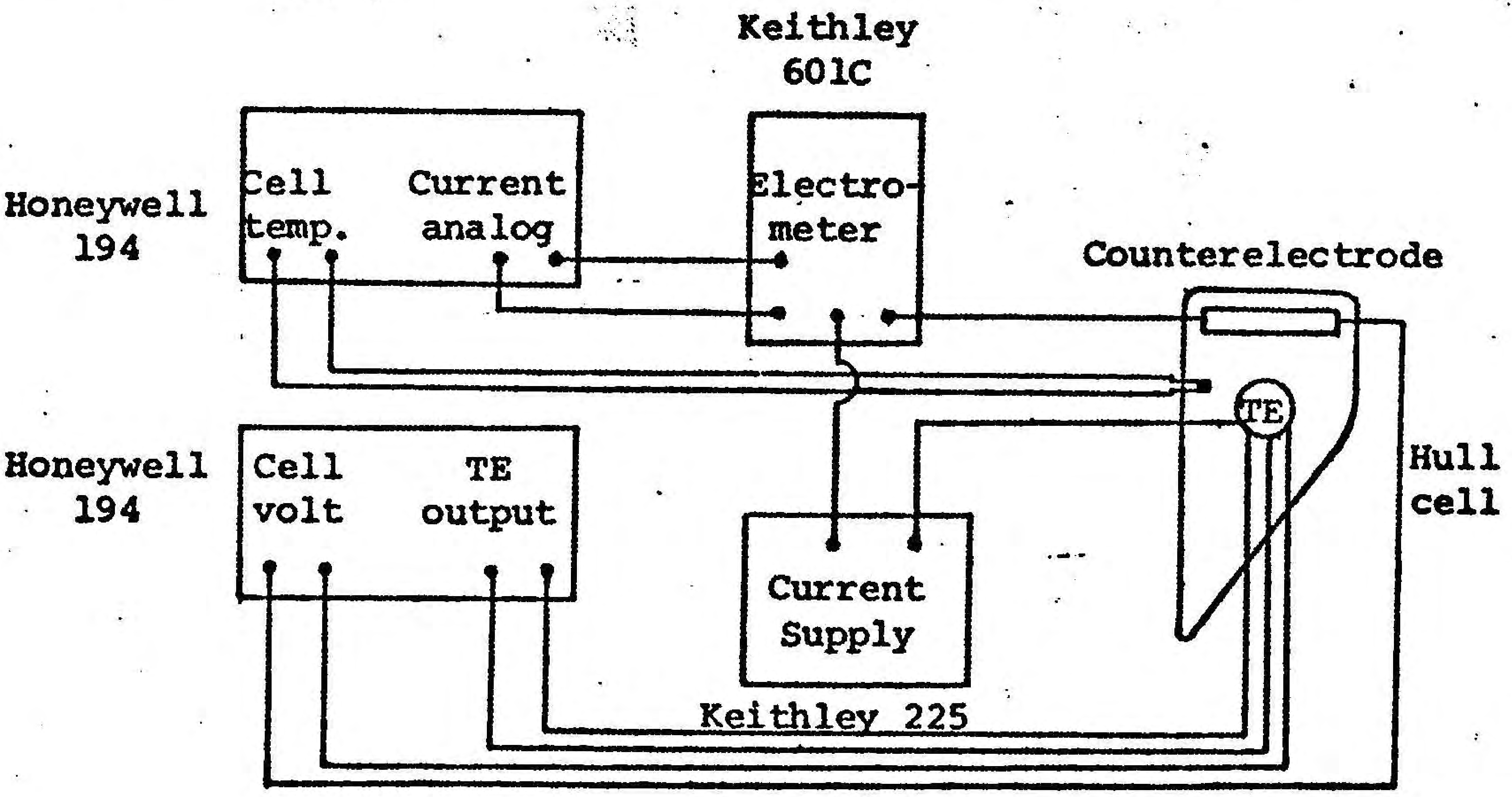

Fig. VII,4,b - Circuit diagram of the apparatus shown in Fig. VII,4.

the wires and the bead. The various components of the TE and the overall assembly shown in Fig. VII,5, are described in the caption of Fig. VII,6. This thermoelectrode was manufactured commercially according to the specification given in Fig. VII,6.

The immersed test surface area of the small TE was taken as equal to 0.1 mm^2. This value was obtained by several methods of estimation: by the use of current density voltage plot for copper plating, by optical microscope measurements, subsequently confirmed by photographic enlargements of the TE stripped of its electrical isolator, (Fig. VII,7). Therefore, the values of current density indicated in the experimental results are based on this surface area.

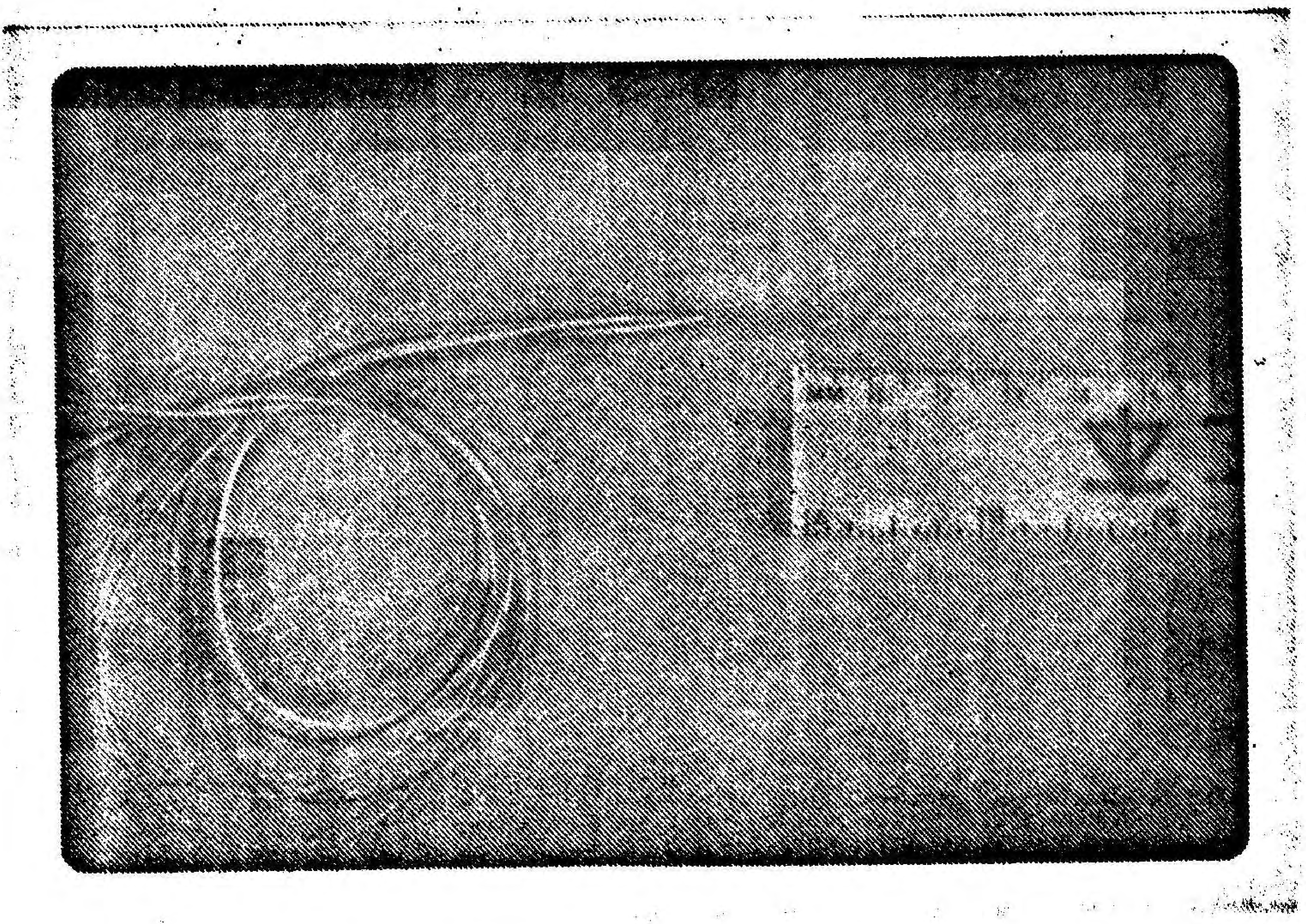

Fig. VII,5 - Thermoelectrode Overall Assembly

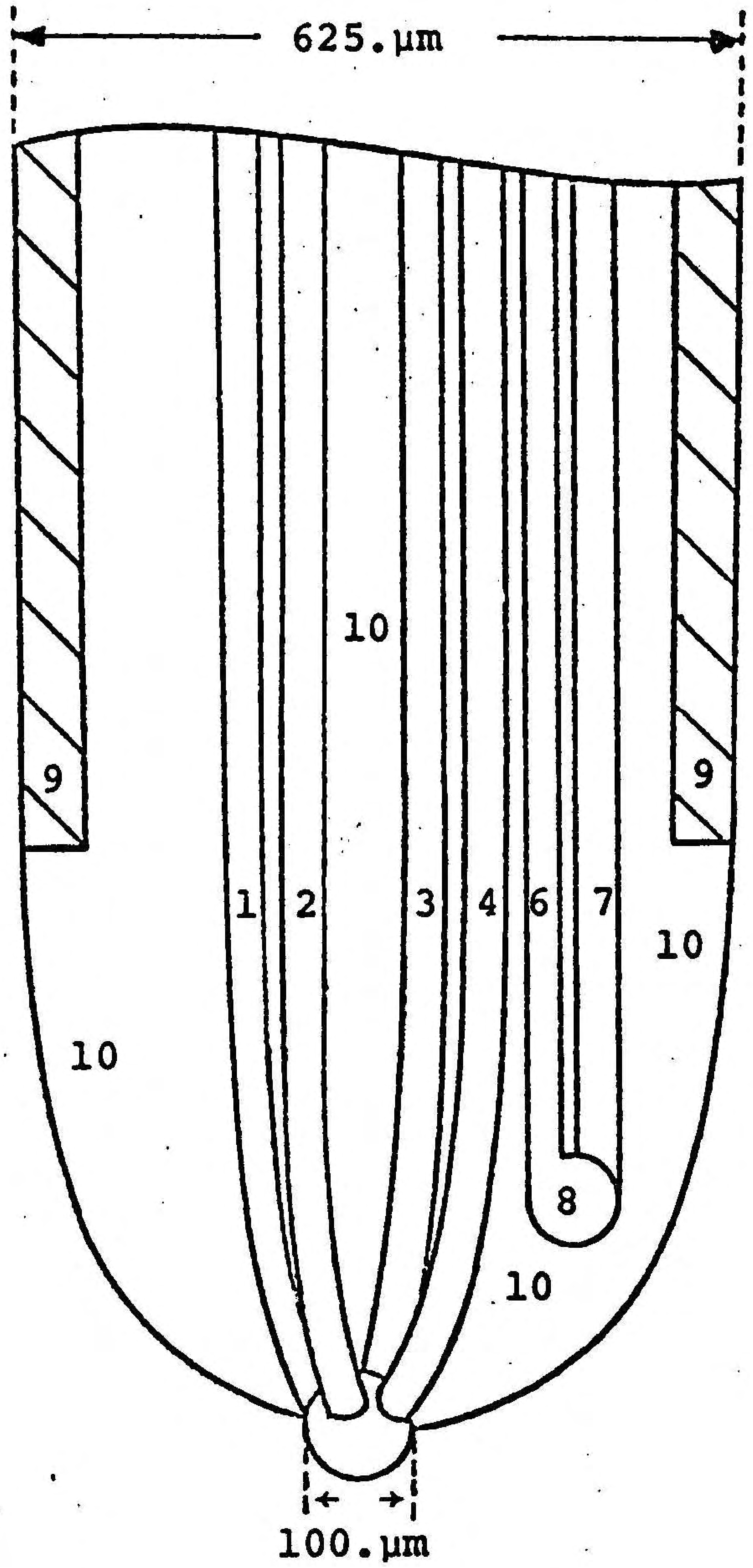

Fig. VII,6 - Ideal geometrical configuration for small TE.

N°	Description	Color (Fig.VII,5)
1	Pt-13%Rh,25.µm diameter wire	wht
2	Pt " " "	red/wht
3	Pt " " "	grn/wht
4	Pt " " "	blk/wht
5	Exposed hemisphere of electrode test surface	
6	Pt 25.µm diameter wire	red
7	Pt-13%Rh, " " "	blk
8	Reference electrically isolated junction	
9	Pt-13%Rh Sheath	
10	Electrical isolator	

Fig. VII,7 - Small thermoelectrode, magnification 50X; the sheath diameter is 0.625 mm and the four-wire bead test electrode is 0.250 mm diameter.

C. PROCEDURE AND RESULTS

1. Specific Procedure

The procedural aspects particular to this investigation, besides those common to electrochemical experimentation, were the following.

After calibration, the wire which produced the highest SS effect between PtA and PtB in Fig. VII,2, was used to measure the cell voltage and the other was connected to the current lead.

The TE test surface was pretreated in each experiment, in order to have two kinds of constant initial surface conditions. This was performed in 1 n H_2SO_4 aqueous solution either evolving hydrogen on the TE at 50. mA cm^{-2} for approximately 10 min, or oxygen at 5. mA cm^{-2} for the same length of time.

The composition of the electrolyte was maintained at values similar to those indicated in section VI,B,1; that is, 1,000 g of water, 1. g-mol $MeSO_4$, and 1. N H_2SO_4; all chemicals used were of analytical reagent grade.

The temperature of each experiment is indicated with the results and were in the range 18-30°C, measured 5. mm below the electrolyte surface.

The sequence of modes followed in most runs was:

1) cathodic plating of the metal under consideration on the pretreated TE surface;

2) open circuit for approximately 1. s;

3) anodic stripping of the metal from the TE;

4) short circuit of the cell, from here on called 'Galvani' mode.

In the large TE series of experiments the power supply available did not permit a satisfactory control of the current. However, this was subsequently remedied during the experiments with the small TE by use of the current source which was then available.

2. Results for Large Thermoelectrodes

Six TEs with the characteristics indicated in Fig. VII,2 were constructed and experimented on three systems: copper, iron, and hydrogen and oxygen.

Fig. VII,8 shows a reproduction of the results generally obtained for the cathodic deposition of copper with hydrogen co-evolution. The speed of the strip chart of the recorder was 1. in/sec. Fig. VII,9 refers to the anodic dissolution of copper and oxygen evolution when the copper had been entirely stripped from the TE.

Fig. VII,10 reproduces the results obtained for the iron system using the same apparatus as before, only with $FeSO_4$ replacing $CuSO_4$ in the electrolyte, and Fe counter-electrode replacing the Cu one. Cathodic deposition and anodic stripping of iron and gaseous co-evolution are shown together in this figure.

With the same apparatus and conditions as for the previous experiments, but without metal sulphate in the electrolyte, and with a flat platinum foil of 10. cm^2 of immersed area as the counterelectrode, hydrogen and oxygen were evolved on the TE. Fig. VII,11 reports the typical results.

In order to see if the ion concentration in the bulk has any effect on the microvolt readings, an electrolyte of two normal H_2SO_4 was investigated under the same conditions as

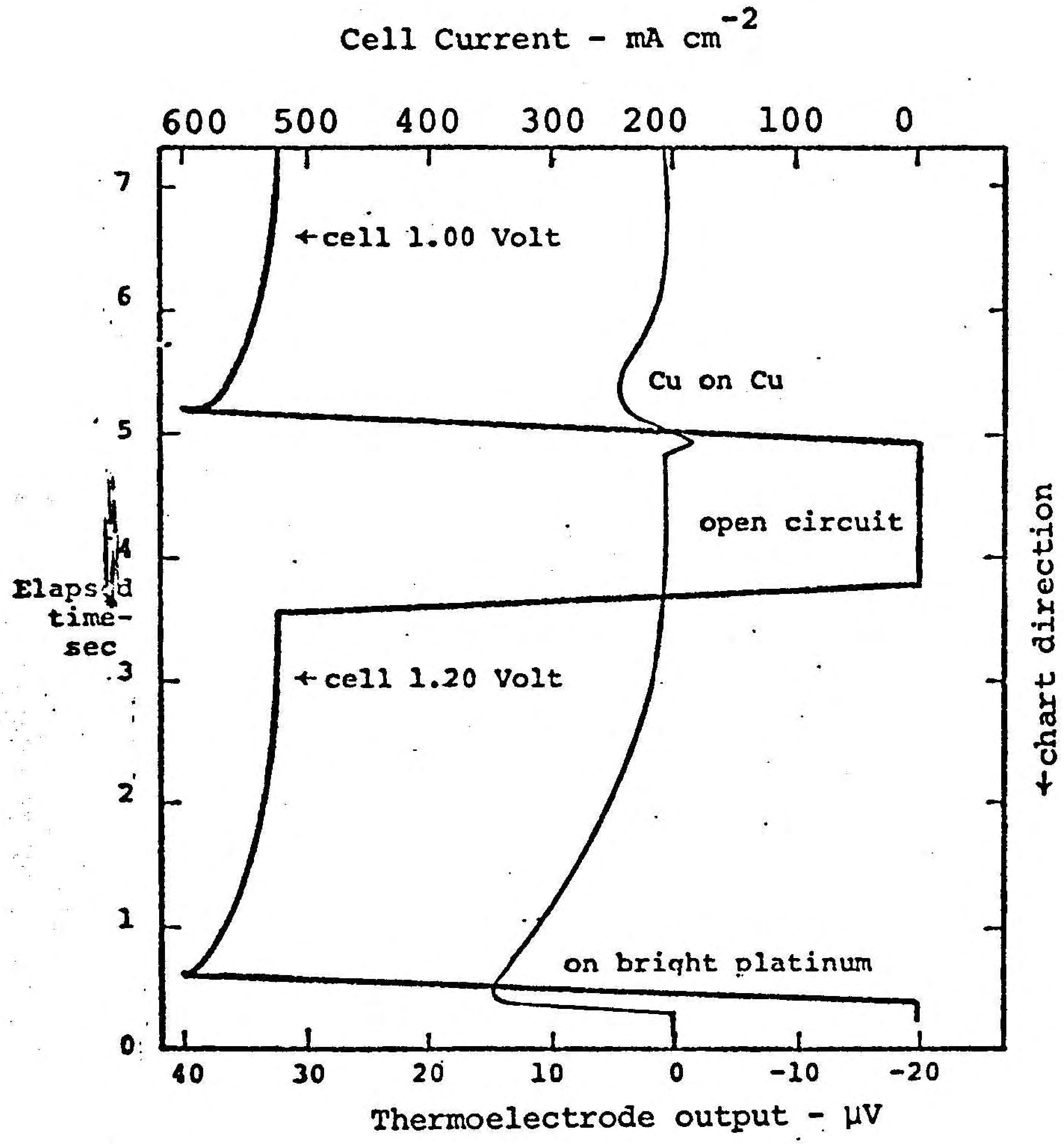

Fig. VII,8 - Copper deposition on large TE. Thick line refers to cell current; the thin one to the microvolt readings.

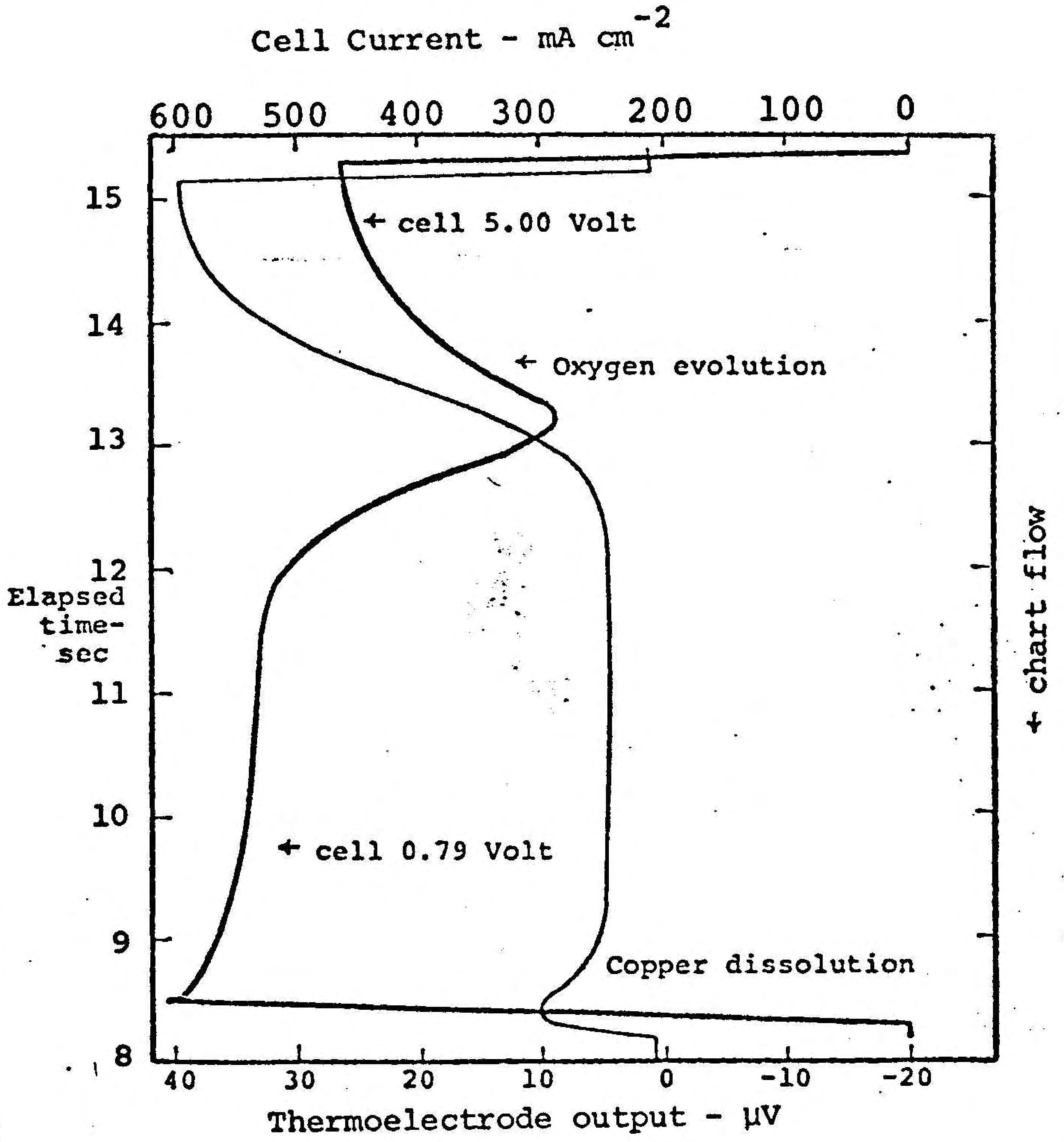

Fig. VII,9 - Copper stripping from large TE and oxygen evolution. The thick line is cell current while the thin one refers to microvolt readings.

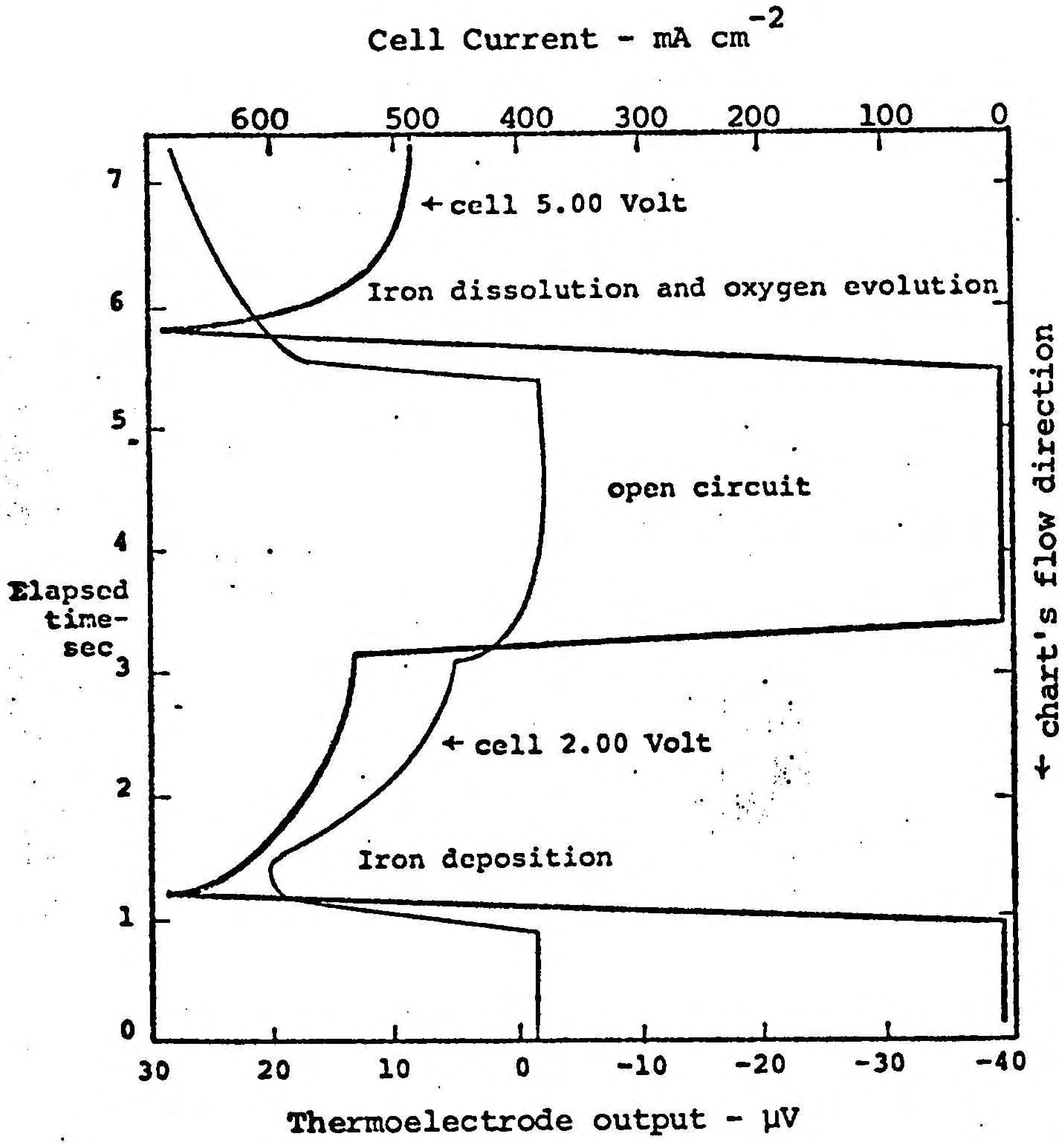

Fig. VII,10 - Iron deposition and stripping on large TE. The thick line is cell current and the thin one microvolt.

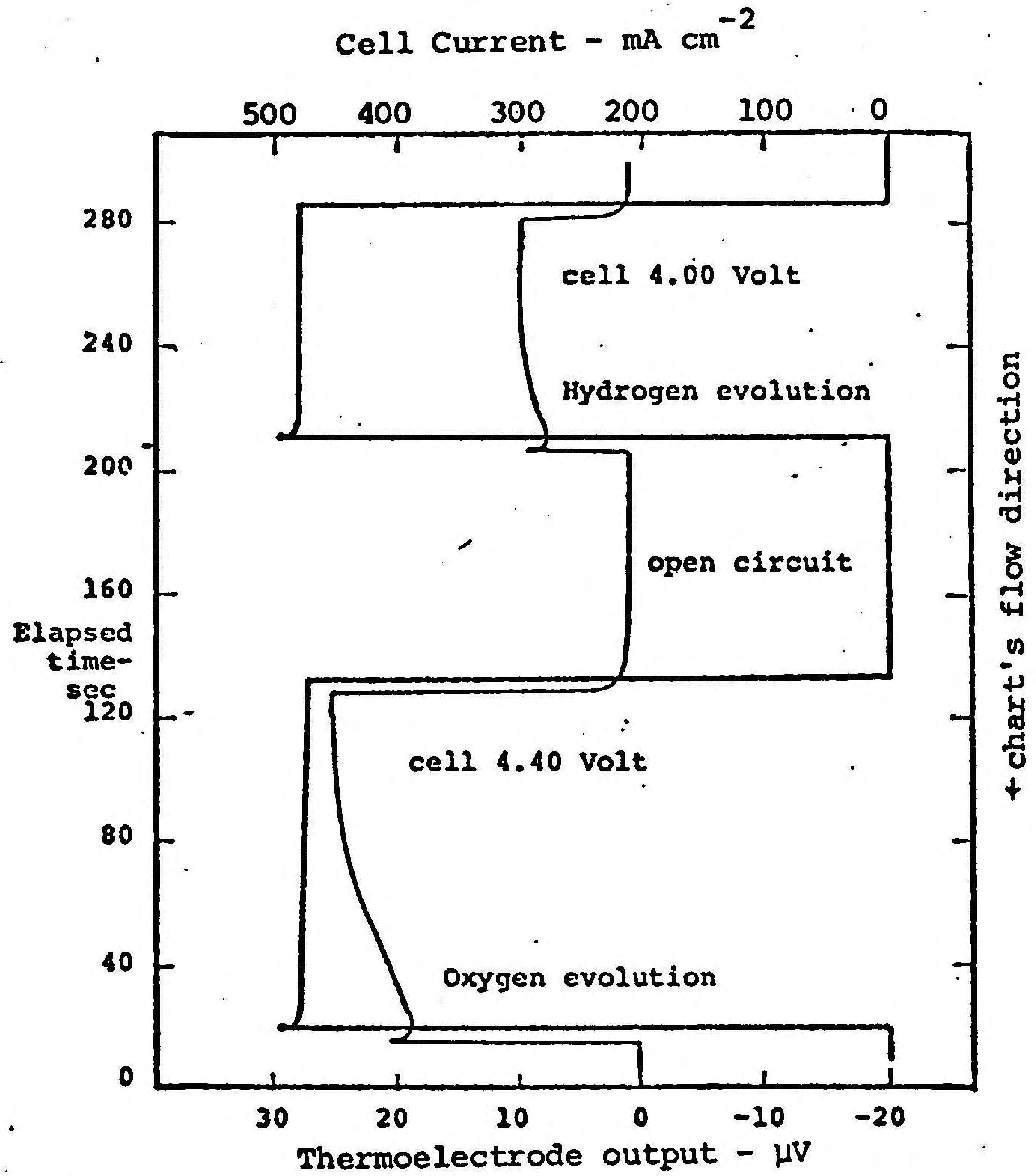

Fig. VII,11 - Oxygen and hydrogen evolution on large TE. The thick line is cell current and the thin one microvolt.

above. The results showed no effect from the H^+ concentration in the bulk on the microvolt readings.

The temperature had the following effect. A higher temperature of the electrolyte produced lower microvolt readings. In particular at an electrolyte temperature of 27.0°C the oxygen evolution reading was 21. μV, while for the hydrogen the value was 10-11. μV. At 32.°C the value for the oxygen reduced to 19. μV, while for hydrogen it decreased to 7-8. μV.

3. Results for Small Thermoelectrodes

Six TEs with the characteristics indicated in Fig. VII,6 were constructed by welding with miniature oxygen-acetylene torch, and one by spark welding.

Fig. VII,12 shows photographs of the recorded charts as they were typically produced in hydrogen and oxygen systems, as a function of current density. The CE metal was lead.

Fig. VII,13 shows the output in the case of copper as it was typically produced as a function of current density.

Fig. VII,14 shows the results for nickel.

It is appropriate to stress that the adverb 'typically' should have been replaced by 'always' because the reproducibility of the results was satisfactory, as it is shown in Fig. VII,14,b in which a double run is depicted. Finally, other data from the same series of experiments depicted in Fig. VII,12,13,14 are given in Table VII,1.

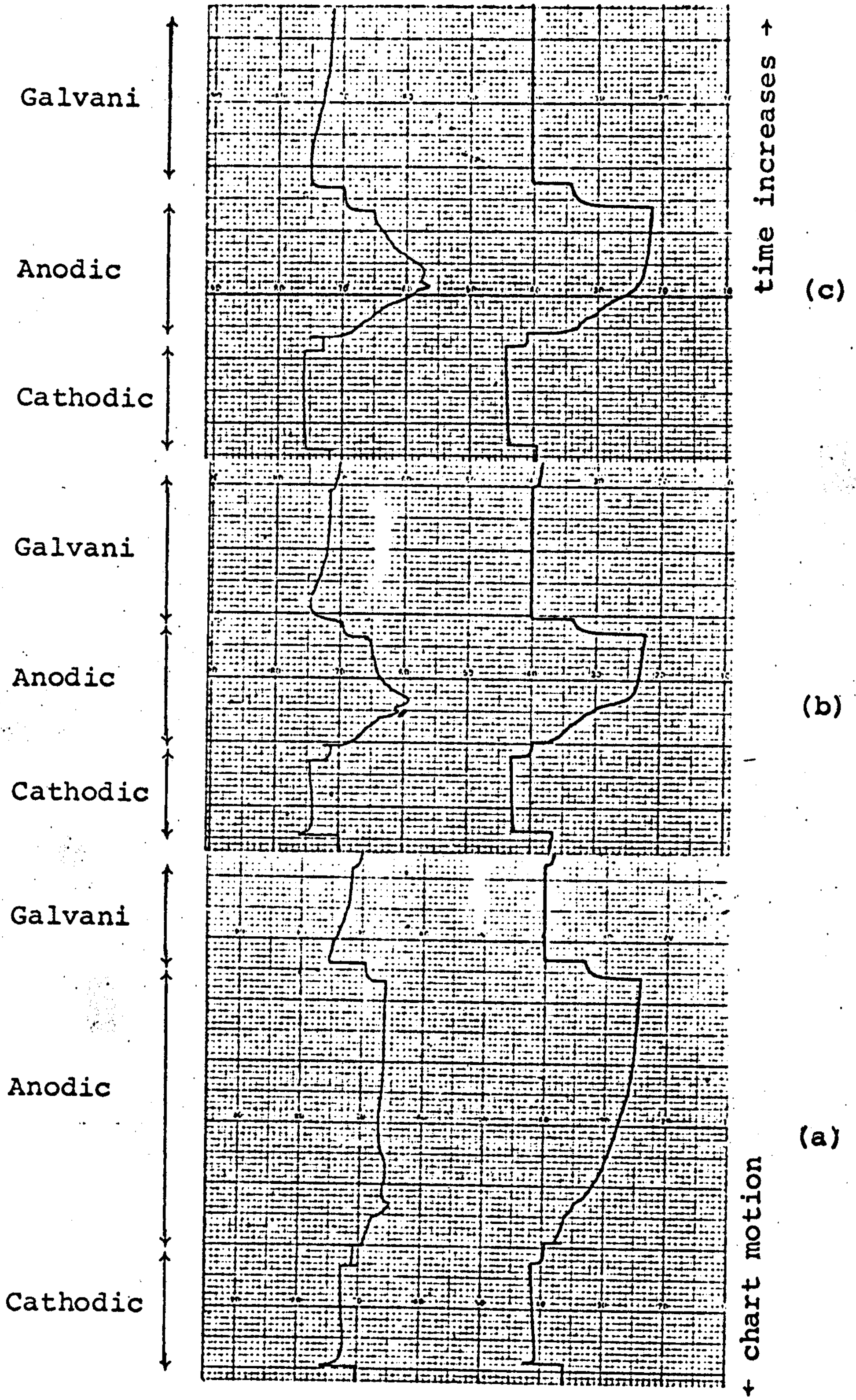

Fig. VII,12 - Hydrogen and Oxygen evolution in aqueous solution 1 N H_2SO_4, 23°C; TE output on the left at 1.μV per division; total cell voltage is on the right at 0.1 V per division.

	(a)	(b)	(c)
Current ~~Density~~: mA cm^{-2}	10	25	50
Chart Speed: s per division	2	2	1

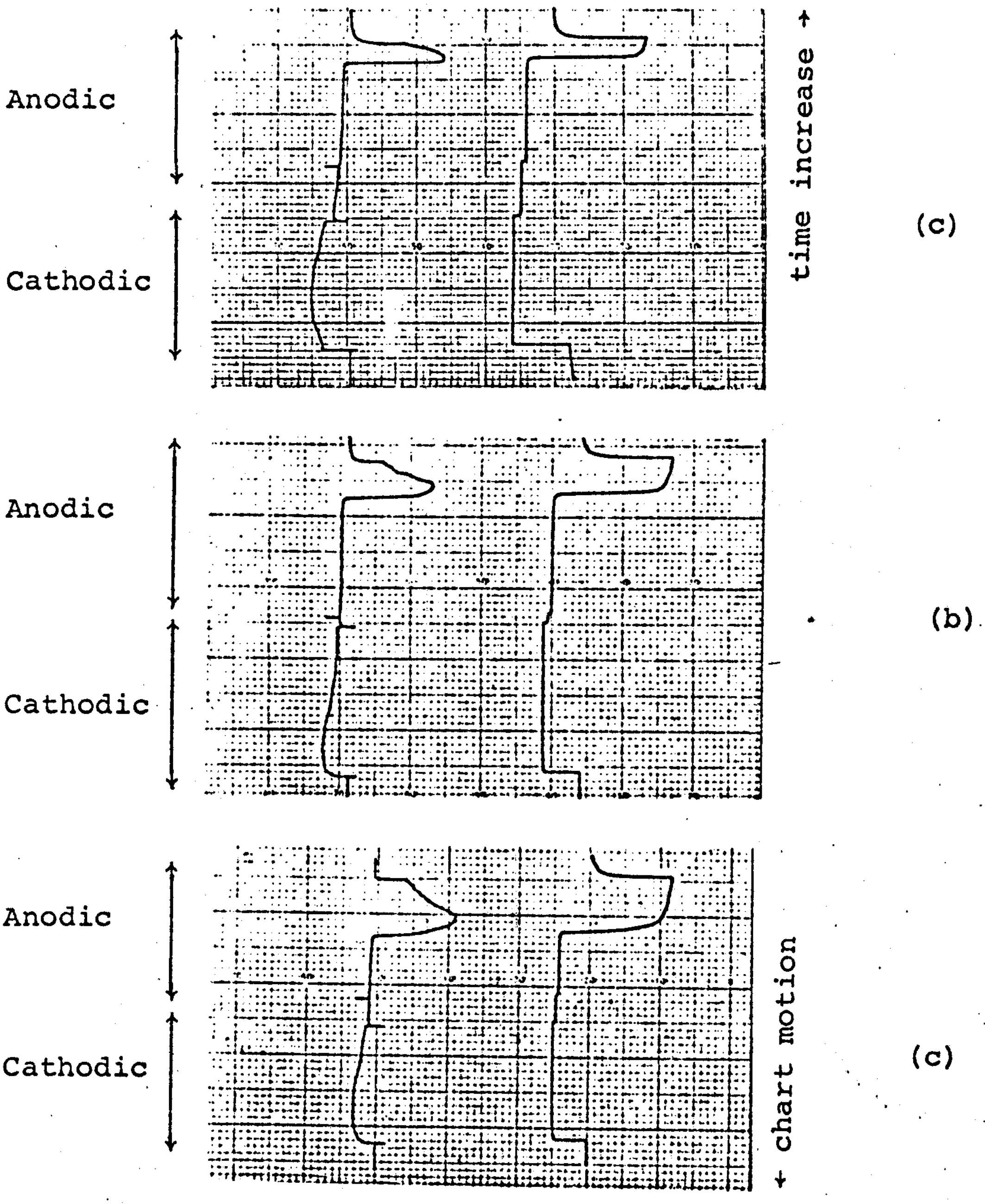

Fig. VII,13 - Copper deposition and dissolution in 1 M sulfate aqueous solution, 1 N H_2SO_4 23°C; TE output on the left: 1.μV per division; total cell voltage on the right: 0.1 V per division. Chart speed: 2. s per division. Current density: (a) 25. mA cm^{-2}, (b) 50. mA cm^{-2} (c) 100. mA cm^{-2}.

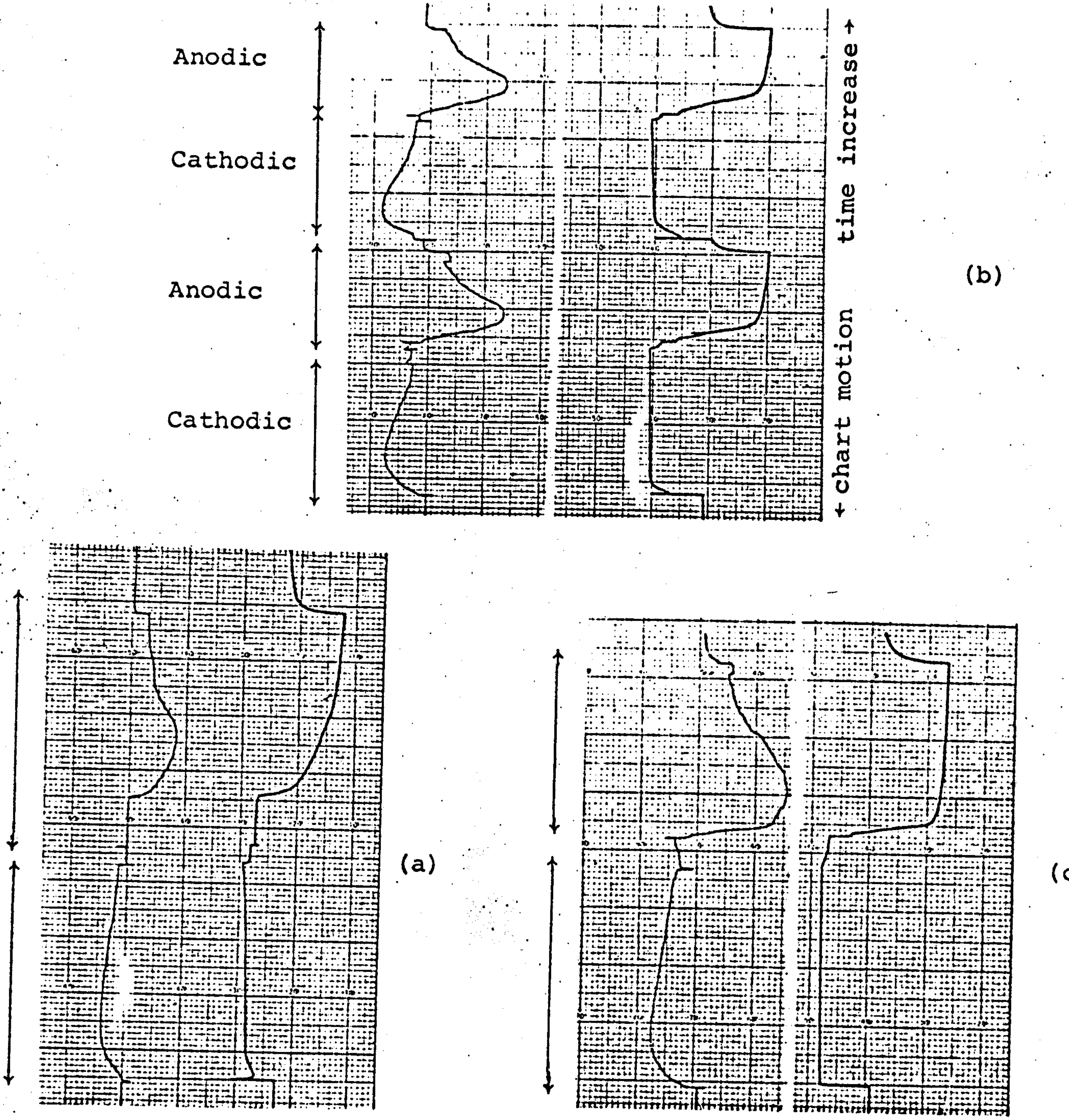

Fig. VII,14 - Nickel deposition and dissolution in 1 M sulfate aqueous solution, 1 N H_2SO_4; TE output is on the left at 1.μV per division; total cell voltage is on the right at 0.1 V per division.

	Current mA cm^{-2}	Temp. °C	Speed s per div.
(a)	15	26	1
(b)	30	22.5	2
(c)	60	22.5	0.5

Table VII,1

Thermoelectrode Output

C : cathodic mode, excess energy (positive value)

A : anodic mode, anodic cooling (negative value)

Current Density	$H_2 - O_2$		Copper		Nickel	
	C	A	C	A	C	A
$mA\ cm^{-2}$	(+) μV	(-)	(+) μV	(-)	(+) μV	(-)
5	1.5	2.0	2.0	0.0	2.5	4.0
10	3.0	6.0	2.0	0.0	4.5	6.5
15	3.5	7.5	2.0	0.0	4.0	8.0
20	4.0	10.0	3.5	0.0	6.5	14.0
25	4.5	12.0	3.5	0.1		
30	4.5	13.0	3.7	0.2	7.5	16.0
35	5.0	15.0				
40	5.0	15.5	4.0	0.3		
50	5.0	16.5	4.0	0.5	8.5	15.0
60					8.5	19.5
70						
80			4.5	0.5		
90						
100			5.5	0.8		

D. DISCUSSION OF THE EXPERIMENTAL RESULTS

1. Introduction

As indicated in the introductory chapter, the aim of this experimental investigation is to confirm, with semi-quantitative experimental results, the qualitative interpretation of works in the literature and the quantitative analysis of the electrodynamic model. Therefore, no attempt will be made to produce precise values for the variables involved, but the author's estimation is obtained through a semiquantitative analysis of the results presented.

2. Observations on the Large TE Results

These results, although severely affected by the parasitic voltage drop (SS effect), are useful for comparing the relative magnitude of the electrochemical effect versus the SS. We have seen that, for the configuration indicated in Fig. VII,2, using PtB as the lead wire, the SS effect shows up as a decrease in microvolt reading.

In Fig. VII,8 copper deposition on the bare TE gives a large emf increase, completely suppressing the SS effect which is opposite in sign. As time proceeds, the copper plated layer becomes thicker and the selvedge moves further away from the TE emf generating region. Thus, the total signal decreases because of the decrease in the electrochemical contribution, while the SS effect, which is an internal constant of opposite sign to the electrochemical effect, will become more prominent.

Further, the presence of the copper plated layer between the TE and the selvedge, not only diminishes the contribution of the interphase process to the reading, but also produces a time lag in the response compared to the SS effect. This time lag is due to the fact that copper has a finite thermal conductivity therefore, the transfer of the excess energy will produce a transient. In fact, we see in Fig. VII,8 that the resumption of the plating, after about a second of interruption, produces a reading which first decreases (SS effect) then increases (Cu excess energy) and finally gradually decreases approaching 0.0 from the positive side.

In Fig. VII,9 showing the anodic stripping of copper, we see the converse of the above described behavior. The SS effect in anodic mode is positive and initially makes a large contribution to the total reading, which, however, decreases with time because of the increasing contribution of the anodic cooling, up to the point at which no copper is left on the TE. Oxygen now starts being de-electronized. At this moment, which will be called the 'oxygen point', we see that the TE output shows a large increase. This is due to the large enthalpy change ($-\Delta H^\circ_{298} = 120.$ kcal/mol O_2[176]) of the reaction of molecular formation of oxygen gas out of the newly formed oxygen atoms. It is noted that the current density decreases, probably due to the formation of PtO_x at the selvedge[177], since, as indicated earlier, the power supply was not altogether satisfactory and could not produce the voltage required to maintain the current.

In Fig. VII,10 we see that the behavior of iron is quite different from that of copper seen previously. The TE output for cathodic deposition on bare TE is larger than for copper; this is primarily due to the large co-evolution of hydrogen gas which, analogously to oxygen, is a reaction with a large enthalpy change ($-\Delta H^\circ_{298} = 104.$kcal/mol H_2[176]). In anodic mode, the dissolution time when only iron is involved, is very short, because this set of electrochemical conditions does not produce adherent iron platings (Fe particles detach from the TE during deposition). The reason, as pointed out earlier, for using these electrochemical conditions, was to achieve uniformity amont the various experiments. Thus, on anodic mode, oxygen evolution begins almost immediately.

Experiments on hydrogen and oxygen electrodes were not originally included in this investigation, primarily because of the complexity of their electrode reactions (adsorption, desorption, atomic-molecular, steps). However, their large energy changes have been very helpful in sustaining the impetus for this investigation during the early stages of the TE development, because their electrode reactions were the only ones to produce readings. Fig. VII,11 reproduces their characteristic behavior at high current density (0.5 A cm^{-2}). The enthalpy change of the oxygen molecular reaction is added to the SS effect contribution; while this effect is subtracted in the hydrogen reading.

Various important observations can be made on secondary results of this series of experiments. It was mentioned in section VII,B,2 that an all platinum (4 Pt wires) electrode was tested as a working electrode in copper system, and that the readings obtained were nearly identical to those of dry calibration. These results, besides confirming that the electrode reactions do not affect the magnitude of the SS effect (which is a function of current and polarity, being constant for a constant current), more importantly, confirms that the changes in recorder output at a constant current density, is really due to emf generated by the electrode reaction occurring at the TE surface.

Further, the TE emf output was found to be independent of the bulk ionic concentration. This fact is in agreement with the concept of excess energy, which in concentrated electrolytic solutions, below the limiting current for smooth deposits, is a function only of the current density.

The study of the effect of changes in the electrolyte temperature will require additional consideration since it involves changes in quantities which are not included in the electrodynamic model; the macroscopic hydrodynamics of the electrolyte next to the interphase is also a function of the cell temperature.

3. Calculation of the Magnitude of Various Thermoelectric Effects Occurring at the TE

Consider the large TE with dimensions and characteristics as indicated in Fig. VII,2 with a current density I of 0.5 A cm^{-2}.

The Joule heat is:

$$H_J = I^2R \qquad (J\ s^{-1}\ cm^{-3})$$

Since the bead was obtained by welding the three pure platinum wires and the Pt-13%Rh wire together, then, if the bead is considered to be homogeneous, the Rhodium content is approximately 3.25%. Further, assuming it is permissible to linearly interpolate between the values of resistivity of pure platinum (9.83 μΩ cm) and of Pt-13%Rh (19.0 μΩ cm), then 12.5 μΩ can be taken as representative of the TE average resistivity. Since the TE bead is 1. mm in diameter, the bead cross sectional area is 3.14 mm^2, the current density will be 1.5 A cm^{-2}. Then:

$$H_J = (1.5)^2(1.25x10^{-5}) = 2.8x10^{-5}\ J\ s^{-1}cm^{-3}.$$

The Peltier effect is: $H_P = \varepsilon\, T\, I \quad (J\ s^{-1}cm^{-2})$

and we have two of these effects on the TE under metal deposition and dissolution:

1) Pt, Pt-13%Rh with temperature coefficient of $6.0\ \mu V\ °K^{-1}$

2) Pt, Cu (for example) temperature coefficient of $7.6\ \mu V\ °K^{-1}$,

in the temperature range of 20-30°C. Then:

$$H_{P1} = (6.0x10^{-6})\ (300)\ (1.5) = 2.7x10^{-3}\quad J\ s^{-1}cm^{-2}.$$

$$H_{P2} = (7.6x10^{-6})\ (300)\ (1.5) = 3.42x10^{-3}\quad J\ s^{-1}cm^{-2}.$$

The Thomson effect is:

$$H_T = -\mu_T\ I\ \frac{dT}{dx}\qquad J\ s^{-1}cm^{-3}$$

where:

μ_T : Thomson coefficient

dT/dx : thermal gradient through the bead.

The largest reading obtained in the results for large TE was for the oxygen evolution, about 40. μV in Fig. VII,9, which corresponds to 6.66 °K of temperature increase. For platinum:

$$\mu_T = -12\mu V°K^{-1}\qquad \frac{dT}{dx} = \frac{6.66\ K°}{.1cm}$$

assuming a linear thermal gradient. Thus:

$$H_T = (12x10^{-6})\ (1.5)\ (6.66)/(0.1) = 1.19x10^{-3}\quad J\ s^{-1}cm^{-3}$$

However, this result may be too large since the temperature difference probably extends up the wires as well.

In summary, these thermoelectric effects have, cumulatively, a maximum order of magnitude of $10^{-3}\ J\ s^{-1}cm^{-1}$ which is small when compared with the values obtained with global thermodynamics (10^{-2}J $s^{-1}cm^{-2}$ in section VI,F,2), and even smaller compared with the magnitude of the excess energy of the electrodynamic model (10^{-1}J $s^{-1}cm^{-2}$ in section VI,E,4).

Therefore, at this stage of development of the thermoelectrode we are justified in considering these effects as negligible. This is even more true, as far as the results obtained with the small TE are concerned, since the current density used in those experiments was an order of magnitude lower than for large TE.

4. Analysis of Small TE Results

The quality of the results obtained with the small TEs permits a semiquantitative analysis of the results as a function of current density and allows for the differentiation among the various electrode reactions.

Fig. VII,12 indicates the improved sensitivity of the TE to the different types of reaction energetics. The current was recorded on a separate chart, instead of together with the TE output as was done in the large TE tests since as indicated previously, the apparatus which was now used allowed density to be maintained constant at the value indicated throughout the experiment. Instead, the total cell voltage was recorded on the same chart as the TE emf output, and at a scale and polarity which gave pen movements of the same order of magnitude. This was done primarily to demonstrate the independence of the TE reading on the cell voltage.

Each of the graphs (a,b,c) of Fig. VII,12 represent the sequence, cathodic, open circuit, anodic, open circuit, Galvani modes. The Galvani mode, in which the cell was short circuited, was used to determine when the TE surface conditions were sufficiently stabilized for the next run to start, as well as the location on the chart of the 0.0 V for the total cell voltage. It is worth noting that this procedure gives additional evidence of the degree of sensitivity of the small TE. Since the chart was flowing downward, the graphs of Fig. VII,12 have been placed in order of increasing current density from bottom to top of the page. However, the graphs do not represent experimental results obtained in the immediate sequence, instead, these graphs have been taken from different experiments since the reproducibility was satisfactory. Starting with graph (a), representing the results at low current density (10. mA cm^{-2}), it can be seen that the cathodic mode which results in hydrogen evolution produces an emf of about +3μV with a gradual approach to steady state. The initial peak corresponds to the instant at which the current is switched on; this was the only time when the source could not completely control the current. After about six seconds of open circuit, the anodic mode was started. An initial slow decrease, followed by a dip to a minimum of -5μV back to a steady state of about -4μV can be observed. After another six seconds of open circuit, the cell was short circuited - Galvani mode.

The cell total voltage is observed at 0.0 V while the TE output is at a value of +6μV. It is interesting to note that this value is equal to the cathodic initial peak corresponding to the current which the power supply could not control. This Galvani reading gradually decreases, returning to the original 0.0 V upon reopening the circuit. Graph (b) of Fig. VII,12 shows the effect of increased current density (25. mA cm^{-2}) on the TE output. We see that the initial cathodic peak has the same magnitude as in graph (a) -- about +6μV. However, the cathodic steady state is reached at +4μV. The Galvani mode shows a similar behavior as for the previous graph, but with a slightly longer time during which the reading is at the maximum value. Graph (c) shows the same features but the profile is of a higher magnitude because of the higher current density (50. mA cm^{-2}). The +6μV of cathodic steady state dwarfed the initial peak, and the anodic dip reaches -16μV, maintaining however the same characteristic profile as before. The Galvani mode still has the same +5μV of maximum value but the time of its natural duration is longer. This is a consequence of having used a larger current density (twice as much as the previous run) for the same length of time, which changed the electrode surface characteristics to a larger extent; therefore, the Coulomb requirement to return to the natural equilibrium characteristics of the surface is larger. The characteristic peak of the anodic minimum which lasts approximately one second, may indicate that a particular reaction

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Fig. VII,13 reports a similar series of experiments conducted with the copper system. Graph (a) shows the typical reading obtained for 25. mA cm^{-2}. In this system, the 0.0 V of the total cell voltage can be read after the cathodic period has occurred, that is, when the TE is plated with copper and the surface is thus the same as the counterelectrode. Thus, the Galvani mode is not appropriate and therefore was not tested. As pointed out during the discussion of the results for large TEs, the anodic behavior consists of a slight decrease at first, then when the copper has been entirely stripped, a deep minimum of -14μV is reached. At this point, the oxygen point, the PtO_x layer on TE forms, followed by the oxygen gaseous evolution which causes the readings to increase again. Graph (b) and (c) show the progressive increase in magnitude of the emf output along with the increase in current density (+5.5μV at 100 mA cm^{-1}).

Finally, Fig. VII,14 shows the results obtained for the nickel system, which are clearly different from those for copper. The first difference is the cathodic rise which has a lower rate but reaches a higher maximum (in graph (b) +8μV for the 30 mA cm^{-2} range). The second difference is in the shape of the oxygen point; it is more gradual than for copper. This may indicate the formation of some nickel hydroxide.

Fig. VII,14,b reports the results of two runs obtained in immediate succession, and has been included to show the degree of reproducibility of these results.

5. Interpretation of the Results in Terms of the Electrodynamic Model

When we consider the experimental results just presented in the light of the electrodynamic model, the following agreements may be observed.

First, the electrodynamic model predicts for cathodic electrode processes of electronation in general, that the energy released by the de-excitation of the newly formed species is transferred, through the selvedge, thereby increasing the energy density of this region, to the metal bulk.

Now, since the generation of a positive emf output by the thermoelectric element used, is indication of an increase in the energy density of the region surrounding the junction, we can see that the model prediction of the (sign) direction of the energy change is correct. However, the magnitude of the energy change, as measured by the small TE (10^1°K) is very much smaller than the magnitude calculated in terms of the electrodynamic model in section VI,E,4 (10^5°K), thus 10^4 times smaller.

This fact can be explained by comparing the size of the selvedge (actually the width of the layer of the newly deposited atoms) with that of the metal bulk. In the case of the small TE, under cathodic deposition of copper for example, the growth of the deposit, that is the selvedge motion toward the electrolyte, can be estimated as shown below by considering the following:

Taking the diameter of a copper atom to be 2.55 Å, then the planar density (assuming cubic arrangement) is:

$$1\text{x}10^{16}\text{Å}^2\ \text{cm}^{-2}/(2.55)^2\text{Å}^2 = 1.5378\text{x}10^{15}\ \text{copper atoms cm}^{-2}.$$

A current density of 100 mA cm^{-2} (this is within the range used in the experimental runs) is equivalent to 0.1 C $\text{s}^{-1}\text{cm}^{-2}$ and since a Coulomb is equal to $6.24\text{x}10^{18}$ e^-, then the electron flux is:

$$0.1 \times 6.24\text{x}10^{18} = 6.24\text{x}10^{17}\ e^-\ \text{s}^{-1}\text{cm}^{-2}.$$

Since $2e^-$ are required for each Cu^{++}, then the equivalent flux of copper atom is:

$$6.24\text{x}10^{17}/2 = 3.12\text{x}10^{17}\ \text{Cu}^\circ\ \text{s}^{-1}\text{cm}^{-2}.$$

Consequently, there will be:

$$3.12\text{x}10^{17}/1.5378\text{x}10^{15} = 202.93\ \text{layers of copper per sec.}$$

Therefore, the deposit gross of the rate of:

$$202.93 \times 2.55 \simeq 5\times10^2 \text{ Å s}^{-1}.$$

Recalling that the TE bead radius was 125. μm (Fig. VII,7) or 1.25×10^6 Å, we can see that after one second of deposition the thickness of the copper layer is approximately 10^4 times smaller than the radius of the bead. Perhaps a better appreciation between these two quantities may be had by considering the relation between one centimeter and one kilometer.

Consequently, since this relation between the dimensions is of a comparable order of magnitude with the relation between the calculated and measured energy densities, we also can say that the magnitude of the energy changes as predicted by the electrodynamic model is correct.

Further, the reason for the comparatively large emf output generated by the evolution of gases, as indicated in section VII,D.2, is the additional energy released by the reaction of molecular formation out of the newly reduced atoms at the selvedge surface. In the case of hydrogen, 104. kcal mol^{-1} or 4.5 eV/molecule are added to the 27.0 eV of de-ionization of two protons. Therefore, since this additional energy must also be transferred to a third body (the selvedge), otherwise the molecule will be in an excited state and will decompose. Thus, the electrodynamic model predicts an emf generation which is larger for hydrogen than for copper which has a comparable de-ionization energy for the same number of Coulomb. Consequently, this prediction is also correct.

The comparison between the magnitudes of the emf output of nickel and copper, under the same electrochemical conditions, shows a larger output for nickel than for copper. If this is in agreement with the commonly experienced higher degree of difficulty in plating smooth nickel than smooth copper, at first sight it may appear to disagree with the predictions of the electrodynamic model as discussed in section VII,A,3, for which copper having a larger value of de-ionization energy (28.0 eV) than nickel (25.8 eV) should produce a larger emf reading. However, the electrodynamic model is still a simplified representation of reality, and the numerical analysis performed in the previous chapter of the case of copper included only the de-ionization energy. As indicated in the development chapter, only a simple electronation reaction was considered, without accounts for the energy associated with the entropy change, and for side reactions which might simultaneously occur at the electronation interphase. Therefore a tentative explanation should consider the possible formation of nickel hydroxide (about 100. kcal/mol[171]) after the metal has been deposited.

At this point, it would not be inappropriate to reiterate that electrode processes are very complex, consequently, the precise analysis of their energy changes occurring at the interphase will require large amounts of additional theoretical development and related experimental work.

This section will be concluded with a few considerations on the phenomenon of anodic cooling, which to the author's knowledge, represent the first experimental evidence of its existence. In the case of copper for example, we see that after all the copper previously deposited on the TE has been dissolved, a much larger overpotential is required in order to de-electronize oxygen. Thus, the electron plane (Fig. V,1) is driven further inside the selvedge, leaving a large region at low energy density. As a result we see that the emf output of the TE becomes more negative, up to the moment at which the first atoms of oxygen arrive to the selvedge to form the six monolayers of platinum oxide. During this occurrence, the emf reading stabilizes at the peak negative value for about one second, as discussed in the preceeding section. Thus, after the completion of the platinum oxide layer, atoms of oxygen start combining to form molecules thereby releasing the enthalpy of reaction, causing the reading to increase (become less negative). Another interesting point which is worth noting, is that the period of stabilization, under the same electrochemical conditions, is larger for the nickel system than for copper. This may indicate the occurrence of reactions other than the PtO_x formation (nickel hydroxide, oxide, etc.).

In summary, the results presented demonstrate that the TE is capable of sensing the reactions occurring at the electrode/electrolyte interphase in terms of energy changes as the selvedge, at the very moment of their occurrence. The interpretation of its output should provide an insight into the complex occurrences which take place during the electrode processes.

6. Significance of the Thermoelectrode and Its Practical Aspects as an Electrochemical Instrument

The thermoelectrode has been a very interesting offspring of this thesis. The development of the instrument has been a direct result of the search for an experimental apparatus capable of measuring energy changes at the metal side of the electrode/electrolyte interphase.

From the results and their discussion presented in this chapter, it is apparent that the TE has the potential of being used as an analytical instrument when calibration under a fixed set of electrochemical conditions has been established. The output of the TE can then be regarded as a "thermoelectrogram" characteristic of the particular electrode process. Moreover, it can be used to test the effects of impurities, additives, etc., on the electrode reactions.

In fact, some of the extemporaneous results, which were not reported in the results section, included experiments with organic additives generally used in electrolytic industrial operations; namely, thiourea and dextrin. These substances added during the process of a regular copper cathodic mode generated an increase in the emf output of magnitude comparable to the normal reading itself.

However, further development of the sensitivity of the TE, together with semi-emperical correlations of the TE putput with operation variables of interest, is required in order to produce quantitative results. It is envisioned that the thermoelectrode will then prove to be a valuable instrument for direct optimization of electrochemical variables under real, dynamic operational conditions, thereby reducing the need for analytical work in the determination of the performance of industrial operations.

CHAPTER VIII. CONCLUSION

A. EXPLANATION OF INSUFFICIENTLY UNDERSTOOD PHENOMENA IN TERMS OF THE ELECTRODYNAMIC MODEL

An important result of this thesis is the acquired ability of offering precise, simple explanations for poorly understood results of electrode reactions, by using the electrodynamic model.

The confirmation of the existence of excess energy and anotic cooling immediately allows the explanation of the occurrence of temperature dependent phenomena. These have been tabulated and are given below:

1) The fundamental question as to why smooth deposits are obtained at low current density, while as the current density increases the deposit becomes rougher may be explained thus -- the higher the current density, the higher the cathodic selvedge temperature will be, resulting in a larger temperature difference relative to the metal bulk. Thus, the newly formed atoms will undergo a greater amount of structural change.

2) The author's results on the morphology of titanium electrodeposits, reviewed in section II,P, were interpreted as being a function of the metal phase transformation temperature. This can be seen to be correct, since, by operating below the transformation temperature, the cathodic selvedge will crystallize with the high temperature stable structure.

However, upon equilibrating at the lower metal bulk temperature, the deposit undergoes the phase transformation, with the associated structural changes generating localized stresses (tensile or compressive).

3) In connection with 2) it is known that tensile stresses can occur even in the absence of phase transformations. This is possible because of the contraction of the cathodic deposit upon cooling from the selvedge to the metal bulk temperature. There can therefore be random localized fields of tensile and compressive stresses which produce variations in surface energy thereby creating energetically more favorable points for electrodeposition and subsequent dendrite nucleation. The limiting situation arises when the stresses are large enough to produce cracks in the deposit. However, the thermal characteristics of the bulk metal should also be considered, since it determines the rate at which the excess energy is transferred away from the selvedge and can therefore affect the thermal contraction. The thermal characteristics of the metal bulk is discussed further in 4) and 5).

4) The fact that the (111) plane (as reviewed in section II,Q,5) permits the highest current densities is explained by the fact that it has the highest atomic density. This, then corresponds also to the bulk metal orientation with the highest heat conduction per unit surface.

5) An explanation as to why titanium can be smoothly deposited on copper at larger thicknesses than it can be deposited on titanium can now follow. The thermal conduction characteristics of the bulk metal are important in keeping the selvedge temperature at low values. The thermal conductivity of copper is over one order of magnitude larger than titanium. Also, the reason for the beneficial effects of current pulses can now be appreciated, since this practice allows time for the excess energy to be transferred to the metal bulk.

6) Galvanoluminescence represents the limiting case of a very large energy density at the selvedge, for which Reynolds and Lumry state, as reviewed in section II,G,2, that products with a large de-excitation energy will be found to emit radiation.

7) The phenomenon of gases overvoltage can be explained in terms of the mechanism for the formation of molecular gas reported by Martins, as reviewed in section II,Q,3; it can be pictured as a sequence of events, in which the initial energy injection (analogue of the selvedge at high temperature) forms an initial small vapor cavity into which the supersaturated solute can be transferred as vapor. In terms of hydrogen overvoltage it can be imagined that the high temperature of the selvedge produces this initial vapor cavity which is immediately filled with molecular hydrogen as a result of the combination of the atomic hydrogen which is supersaturated

in the interphase. Therefore, the higher the cell temperature, a smaller nucleating energy for a given current density is required. In addition, the greater the roughness, the larger the number of high current density, high temperature points.

8) Vagranyan, reviewed in section II,O,3, states that his results indicated that during the deposition of metal, the electrode surface is more active than during its dissolution. This observation is in agreement with the concepts of non-isothermal behavior since the cathodic selvedge has a greater energy density than the anodic.

9) The identity between the values of the exchange currents of solid and liquid Hg and Ga at their melting points, is found by Gerischer and Bockris and Enyo (reviewed in section II,G,3), would also be expected. The reason is that the cathodic and the anodic selvedge will be liquid and solid respectively, when the test electrode was close to its melting point. Further, this structure will not be appreciably changed by varying the bulk temperature by ± 1.°C since the temperature change produced at the electrode is a much larger quantity.

10) Koryushin results on the effect of the direction of the temperature gradient through the cell, reviewed in section II,O,6, where a better deposit was obtained when the cathode was maintained at higher temperature than that of

the rest of the cell may be interpreted in terms of the smaller temperature difference present between the selvedge and the metal bulk. This smaller temperature difference, as discussed previously, produces better deposits.

11) Thouvenin's measurements of his electrolytic Peltier effect, reviewed in section II,0,7, are actually measurements of the energy changes of one electrode. His data represent the overall balance between the promotional energy and the de-excitation energy of the electrode reaction as a whole. The thermoelectrode instead, measures (a) the cathodic de-excitation energy transferred to the metal electrode independently of the promotional energy and (b) the anodic promotional energy transferred to the ionic hydrated complex independeltly of the de-excitation energy. This is the reason why conventional calorimeters cannot be successfully used to measure excess energy or anodic cooling.

12) Yahalom and Zahavi, in section II,0,8, found that the electrolytic crystallization of metal oxides took place at lower temperatures than those for pyrometallurgical crystallization. These observations are a result of the bulk metal (metal strip) being at a lower temperature than the selvedge when the actual crystallization takes place. This bulk dilution effect has also been discussed during the development of the thermoelectrode.

13) An explanation of the beneficial effect of impurities or organic compounds on the morphology of the metal deposits

is rather difficult because of the complexities these substances introduce when they accumulate in the interphase region. It may be possible that they absorb part of the excess energy and return it to the solution, or help the electron transfer by means of their electronic characteristics. However, it is not possible to be definitive in this subject because of the complexity of the behavior of organic molecules under conditions of high temperature and high pressure. Further, theoretical and/or experimental investigations is necessary to resolve this question.

In summary, the preceeding listing of electrode phenomena and their explanations have been included to exemplify the usefulness of the electrodynamic model in the understanding of electrode process behavior and therefore in laying the ground for determining ways to improve them.

B. SUMMARY

The major results of this thesis are the analytical and experimental verification that electrode processes, under conditions of ordinary industrial practice are non-isothermal reactions.

These results have been obtained through the development of the electrodynamic model based on the correct use of potential energy functions, and through the development of the thermoelectrode, an instrument based on the use of thermoelectric effects to monitor the characteristics of electrochemical reactions in progress.

The excess energy and the anodic cooling have been numerically calculated and experimentally measured. It is the author's belief that these two types of data have never been obtained before.

Other indirect results stemming from this thesis have been the ability to offer precise and simple explanations for electrode process phenomena by the use of the electrodynamic model, and the apparent capability of testing sets of electrochemical variables by the use of the thermoelectrode.

C. FUTURE WORK

1. Theoretical

The following are a list of theoretical aspects which are felt to be worthy of consideration:

a) Electrochemical Charge Transfer Coefficient β: The work of Bonnaterre and Cauquis, reviewed in section , deals with the improvements to Marcus' theory by introducing in the expression for α, terms accounting for various electrochemical parameters such as: externally applied potential difference, ionic diffusion coefficient, thickness of double layer, reorganization parameter. The introduction of a term for the selvedge temperature should permit the calculation of values for β in agreement with the experimental data. These would then be the first dynamic values for β ever calculated.

b) Eastman Theory: The introduction into the electrodynamic model of an expression accounting for the energy changes in the form of entropy production and transfer during the electrode process, along the lines indicated by Eastman (reviewed in section II,F) should result in an improved capability to predict precise values of excess energy and anodic cooling.

c) Quantum Chemical Treatment: As was apparent during the review of the most advanced works in the literature, the ultimate approach to the study of electrode processes, which probably has the greatest chances of success of leading breakthrough, is quantum mechanical analysis. Thus, as Bockris writes in a most recent edition[178] "Quantum mechanical treatment of surfaces must be bravely faced".

2. Experimental

There are a number of experimental points which need further investigation and are now presented:

a) Thermoelectrode:

The possibilities of improving the sensitivity of the thermoelectrode have been indicated in section VII,2, thus the maximum practical ratio of surface to volume must be sought along with the best symmetry.

b) Exchange Current Density:

If the above goal of improving the sensitivity of the thermoelectrode is achieved, then, a measure of the value of the exchange current density (at least for the metal/solution systems which have the largest values) could be obtained by correlating the values of the differences between excess energy and anodic cooling at known current densities, with the output of the isolated thermoelectrode. The accomplishment of the above will permit an independent comparison with the values of β calculated as indicated previously. This occurrence should be the first time that the dead circle charge transfer coefficient-exchange current density would have been broken.

c) Thermoelectrodic Series:

A large amount of experimental work is required to establish a listing of the elements in the sequences of their values of excess energy and anodic cooling, as a function of current density. These two series would constitute an ensemble of truly dynamic electrochemical data from which to calculate thermodynamic properties of the elements.

d) Test of Sets of Electrochemical Variables:

The wealth of existing experimental data on the effects of metallic impurities and of organic additives (the works of Gathje[179] and Villas Böas[180] respectively, for example) can be correlated with the output of the thermoelectrode under the same conditions in order to refine the mechanisms responsible for the effects observed.

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