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COMPUTER SIMULATION STUDIES ON
KINETICS OF ELECTRODE SURFACE REACTIONS

by

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in partial fulfillment of the requirements

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TO
MY DEAR
MOTHER and FATHER
and
TZIPI

PREFACE

In the period 1935-1960, work on the kinetics of electrode reactions was centered principally on the study of the rates and mechanisms of overall reactions involved in continuous electrolytic processes, e.g. cathodic H_2 evolution, metal deposition and reduction of organic substances, and anodic processes such as evolution of O_2 or Cl_2 . Although it was appreciated that many of these reactions must involve intermediates, in some cases present in an adsorbed state, the study of the electrochemical reactivity of chemisorbed species at electrode surfaces did not develop very rapidly until 1960, following the development of electronic potentiostats and techniques for potentiodynamic (controlled-potential sweep experiments) examination of surface electrode processes by Will and Knorr⁵⁹. The earliest experimental indication of significant coverage of a Pt electrode by electrodeposited H was reported by Bowden and Rideal⁴⁶ in their studies of capacitance of electrode interfaces by means of charging curves. This was followed by the early controlled-current work of Frumkin and Slygin⁴⁷⁻⁴⁹ in 1935-36 which must be specially mentioned as it was the first in which coverage of a platinized Pt electrode by H was studied in more detail and interpreted in terms of H chemisorption.

The potentiodynamic method was then applied, especially in the period 1960-1970, to many reactions often indiscriminately without sufficient, or any, attention to the complex features of the current-potential behaviour that can arise in surface reactions

involving chemisorbed electroactive or electro-inactive intermediates. A theoretical basis is therefore required to define the kinetic behaviour of various model systems so that experimental results on electrode surface reactions can be both qualitatively and quantitatively interpreted in more satisfactory ways. Some theoretical work has been done previously and is reviewed in Chapter I in the context of the further original work reported later in this thesis.

It is the purpose of this thesis to present the results of simulations of kinetic behaviour of a number of types of surface reactions that take place at electrodes, and deduce the characteristic kinetic features of these processes. In most cases, the results of this approach can be given in exact numerical form and in a few cases in analytical forms.

Several papers have already arisen in this work and have been published. Others are in course of publication. Details are as follows:

- (1) Kinetic and Optical Relaxation Studies of Adsorbed Intermediates in some Electrochemical Reactions, B.E. Conway, H. Angerstein-Kozłowska, F.C. Ho, J. Klinger, B. MacDougall and S. Gottesfeld, Faraday Discussions of the Chemical Society, No. 56, 199 (1973).
- (2) Computer Procedures in Electrochemical Research: Application to Instrument Control, Data Processing and Solution of Complex Kinetic Problems, B.E. Conway, B.V. Tilak, H. Angerstein-Kozłowska, J. Klinger, in Proceedings of the Conference on "Computers in Chemical Research and Education", Ed. D. Hadzi, Elsevier Publ. Co., Amsterdam, 1973.

- (3) Computer Simulation of the Kinetic Behaviour of Surface Reactions Driven by a Linear Potential Sweep - Part I: Model 1-Electron Reaction with a Single Adsorbed Species, H. Angerstein-Kozłowska, J. Klinger and B. E. Conway, J. Electroanal. Chem., 75, 45 (1977).
- (4) Computer Simulation of the Kinetic Behaviour of Surface Reactions Driven by a Linear Potential Sweep - Part II: Sequential Reactions of Adsorbed Species, H. Angerstein-Kozłowska, J. Klinger and B. E. Conway, J. Electroanal. Chem., 75, 61 (1977).

The work on nucleation-controlled processes (Chapter X) is in course of publication. The treatment of surface oxidation reactions as well as the Chapter III, which gives an account of the computational procedures involved in the numerical simulations, will also be published in the near future.

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I wish to express my deep thanks and gratitude to Professor B. E. Conway under whose supervision this work was done. Throughout the course of the research and in the preparation of the thesis, Professor Conway was always willing to devote his time to give advice whenever problems or difficulties were encountered. Also, many interesting and stimulating discussions with Professor Conway, which bore direct impact on the research, made this work possible.

Special thanks are due to Dr. H. Angerstein-Kozłowska under whose immediate direction this work was carried out. Dr. H. Angerstein-Kozłowska was always ready and willing to help, and give her valuable advice, whenever problems arose. Many helpful discussions are appreciated as well.

I wish to thank Dr. L. G. Birta of the Department of Computer Science for introducing me to the simulation programming language "S/360 Continuous System Modeling Program"-(S/360 CSMP). The use of this programme considerably facilitated the computational aspects of this work. Dr. Birta was always willing to give his time to help and proffer advice whenever problems of a computational nature arose with the above mentioned programming language.

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 2. $s = 0.01 \text{ V sec}^{-1}$
 3. $s = 0.005 \text{ V sec}^{-1}$
- (b) $k_1 = k_{-1} = 10 \text{ sec}^{-1}$
1. $s = 0.1 \text{ V sec}^{-1}$
 2. $s = 0.01 \text{ V sec}^{-1}$

(Roman capital pre-subscript numbers, indicating the reaction mechanism in question, have been omitted on the k terms for clarity in this and other diagrams both on the figures and in the captions to the figures.)

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1. $s = 0.1 \text{ V sec}^{-1}$
2. $s = 0.005 \text{ V sec}^{-1}$

(Comparison is to be made with Figs. 5-4 and 5-5)

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Fig.

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$$E_1^{\circ} = E_2^{\circ} = 0.0 \text{ V}, k_1 = k_{-1} = 100 \text{ sec}^{-1},$$

$$k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$$

1. $s = 0.1 \text{ V sec}^{-1}$

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$$k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$$

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2. $s = 0.01 \text{ V sec}^{-1}$

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$$k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$$

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ABSTRACT

Many electrode reactions proceed at metal surfaces with the involvement of one or more chemisorbed intermediates. The surface reactions of, or amongst, these intermediates are often complex.

The various types of kinetic behaviour of a selection of electrochemical surface reactions involving species in monolayers have been numerically simulated for the case where the electrode potential is linearly varied with time (potentiodynamic sweep method). The simulation runs were carried out on an IBM 360 Computer, Model 65, using a simulation language "System/360 Continuous System Modeling Program - (S/360 CSMP)" developed by IBM. A general S/360 CSMP programme capable of solving equations for up to 5 reaction steps in any given overall reaction mechanism was written. The properties of the function generator were embodied in a separate subroutine.

In the work described in the present thesis, which deals with simulation of the kinetic behaviour of various reaction mechanisms, conditions which give rise to particular and characteristic current-potential profiles under different "experimental" conditions for the reaction process in question have been sought. Attention has been focussed on parameters such as the reduced sweep-rate s/k and the ratio of the rate constants governing the individual processes in a given complex reaction mechanism, which in turn give rise to particular shapes of i - V profiles. It is shown that relative values of electrochemical and chemical rate constants, k , interaction parameters, g , and standard

electrode potentials, E° , can be derived using the characteristic kinetic features which are shown to be generated by a given reaction mechanism. Such features are the half-width potentials, $\Delta V_{1/2}$, the peak currents, i_p , the coverage of the chemisorbed species up to the current peak, θ_p , etc.

Where appropriate, comparisons of the simulated kinetic behaviour derived in the present work have been made with experimental results for various systems recorded in the literature.

First, the kinetic behaviour of a single step, 1-e surface reaction is treated theoretically as a simple reference case, especially with regard to: (a) characteristic aspects of its behaviour when significant attractive or repulsive interactions arise between the atoms in the electrodeposited monolayer film and (b) formulation of characteristic features of its kinetic and equilibrium behaviour which provide a reference case for distinguishing the behaviour of other, more complex reactions. The analytical derivations of characteristic parameters, derived previously by some other workers only for Langmuir behaviour, are made more general by extension to cases where two-dimensional interactions are significant.

For surface processes involving parallel steps in which two chemisorbed species are involved, it is shown how a "kinetic relaxation method" can be developed and used for resolution of the behaviour of the two species when the electrochemical reactions in which they are deposited or desorbed occur over the same potential range. This method can be applied when one of the two chemisorbed species behaves more

"irreversibly" than the other. It is shown how experimental results for acetonitrile at Pt electrode obtained by other workers in this laboratory can be treated by this technique.

The potentiodynamic linear sweep method has often been applied to sequential reactions involving at least one chemisorbed intermediate species. The simulation calculations were extended to cases of this kind. The mechanisms which were analyzed involve a first-order chemical surface step coupled with a simple 1-e electrochemical process, thus giving rise to either an "ec" or a "ce" type of overall mechanism. Characteristic features of the kinetic behaviour derived from the computed current-potential profiles were compared with those for the simple 1-e surface reaction case. Holding of the potential, especially at the end of the sweep, proves to be of great importance as it affects the i-V curves obtained on the subsequent reverse sweep in characteristic ways for these types of processes.

The effects of changing the sweep-rate on the kinetic behaviour of a complex reaction having three steps and two chemisorbed intermediates were determined. The three stages are represented by an irreversible dissociative chemisorption step followed by two parallel electrochemical reactions, one of which is considered to be completely reversible while the other is assumed to be totally irreversible. The current-potential profiles for such a case are shown to depend not only on the reduced sweep-rate s/k_3 , where k_3 is the rate constant for the irreversible electrochemical step, but also on the ratio k_1/k_3 , where k_1 is the rate constant for the dissociative chemisorption

reaction (chemical step). The manner in which various ratios of initial coverages of the two chemisorbed species determine the kinetic behaviour characterized by the i - V profiles is noted.

Simulation of a surface oxidation reaction was also attempted by considering a simple "ec" mechanism, where the chemical reaction step was assumed to represent a place-exchange process on the electrode surface; this mechanism is to be compared with the simple 1-e direct electrodeposition reaction mentioned above without a following step. The experimentally observed behaviour that oxide film growth involving a place-exchange reaction obeys a direct logarithmic law, i.e., $q \sim \ln t$, where q is the charge or amount of species which has undergone the rearrangement and t is the time, could not be accounted for. Attention is directed to the fact that the direct logarithmic law, mentioned above, can be mathematically expressed in a more exact way than the inverse logarithmic law, i.e., $\frac{1}{q} \sim -\ln t$. The effect of various holding potentials on the slope of the q vs. $\ln t$ plots is discussed. A general commentary on this problem and possible models for the oxide growth behaviour are given.

A further case, in which a Faradaic process is inhibited by an adsorbed species electrodeposited in a parallel reaction, was investigated. The effect of changing the applied sweep-rate on the Tafel behaviour was demonstrated. Methods are discussed for the determination of the rate constants as well as the values of the two standard electrode potentials from the profiles of V vs. $\log i$.

Growth of a film can also occur by a nucleation-controlled two-dimensional mechanism. Since the potentiodynamic method has been applied experimentally in systems where this type of mechanism could arise, it is important to characterize its behaviour under linear potential sweep control and distinguish it from other possible mechanisms of monolayer growth. Simulations of this nucleation type of mechanism were therefore made for the case of a simple 1-e electrochemical reaction in which film formation occurs by growth from nuclei on the surface.

The kinetic behaviour of this type of process is compared with that of the simple 1-e surface process involving only chemisorption in an ad-layer following either a Langmuir or Temkin type of isotherm. Characteristic parameters which are obtained for the two types of processes are compared and important distinguishing features of the two reactions which emerge are emphasized. The characteristic parameters under various assumed conditions were derived analytically using the statistical approach first discussed by U.R. Evans in 1945 for non-electrochemical cases. The behaviour under potentiostatic conditions was also evaluated for comparative purposes since the potentiostatic method has often been employed for studies of nucleation-controlled reactions at electrode surfaces.

CHAPTER I

INTRODUCTION

1.1 Origin and Significance of Adsorbed Intermediates in Electrode Reactions

Since most primary electrode processes involve gain or loss of an electron, to or from a stable molecular or ionic species, respectively, a single electron-transfer event would normally produce a radical species with a free electron spin or a radical ion. With large conjugated aromatic molecules, such radicals or radical ions are solution-soluble and have been characterized in aprotic media, e.g., by e.s.r., cyclic-voltammetry or ring-disc electrode techniques since their lifetimes are relatively long.

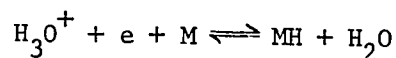
With other reactions involving small ions or molecules, the intermediate resulting from electron-transfer is often stabilized by chemisorption at a transition metal where its odd electron spin is paired with that of electrons in a d-band so that a stable adsorbed state or "surface compound" results. This is the origin of chemisorbed intermediates. In most cases of this kind, the chemisorption takes place in a direct electrodeposition step, i.e., the electron transfer and the chemisorption processes occur simultaneously through a common transition state. In some other cases, a normal metal compound is generated; e.g., with Pb or Hg metal hydrides or metal alkyls are formed.

In the present work, it is the intermediates that are generated in a chemisorbed state that are of interest. For an overall reaction producing an unadsorbed stable product, e.g., H_2 , at least two such events or equivalent reactions producing a chemisorbed species must occur, followed by desorptive recombination or further discharge of a species on to an already

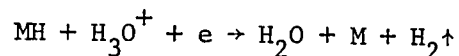
discharged and adsorbed species. Adsorbed intermediates are hence widely involved in many electrochemical reactions.

Typical electrode processes which involve participation of chemisorbed intermediates are the electrochemical gas evolution reactions such as those in which H_2 , O_2 and Cl_2 are produced. Several reaction mechanisms have been proposed for each of these processes involving appropriate adsorbed intermediates. Only representative reaction mechanisms for each case will be exemplified as the main point here is to illustrate the involvement of adsorbed intermediates in the overall processes.

A well-known example is the hydrogen evolution reaction, proceeding by the H atom - H^+ ion desorption mechanism:



followed by

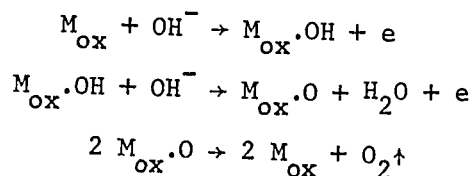


where M represents a metal surface site and MH the H intermediate adsorbed on a metal site M. When H is strongly bound to the metal, as at Pt, full coverage by H can be attained before the reversible- H_2 potential is reached* so that H_2 evolution occurs on a surface fully covered by chemisorbed H. In this case, the kinetically significant intermediate in the reaction mechanism shown above may be a form of H weakly bound on the strongly chemisorbed H layer.

In the case of O_2 evolution a proper stoichiometric formulation of the kinetics of the electrochemical reaction requires at

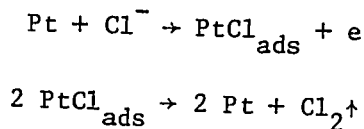
* This is often referred to as "underpotential deposition".

least three steps. A representative example of the reaction mechanism is the following:



occurring in alkaline solutions. The OH and O species represent the intermediate adsorbed species on an oxidized surface (M_{ox}) of the metal since this is normally the situation which arises in anodic oxygen evolution.

The chlorine evolution reaction on Pt surface in acidic media occurs in just two steps involving only one adsorbed intermediate:

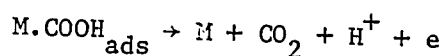
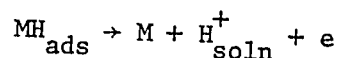
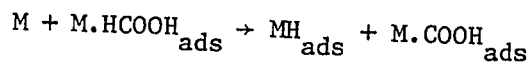
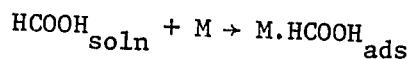


Other types of electrocatalytic reactions involve the dissociative chemisorption of the reactant ion or molecule, followed by electrochemical and often further chemical reactions of the adsorbed intermediates. The characterization of the adsorbed intermediates involved in such oxidations, e.g. of formic acid, methanol and hydrocarbons, has formed an important part of recent literature on electrocatalysis and electrochemical surface science. In a number of reactions, more than one species may be electroactive over the same potential region, a case that will be dealt with later in this thesis.

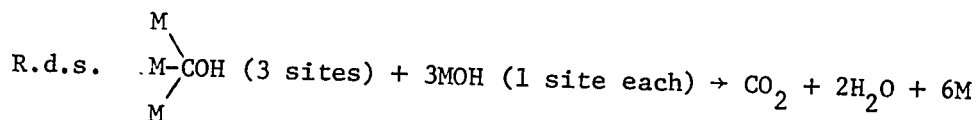
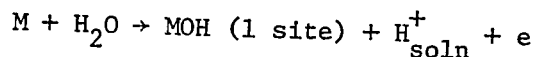
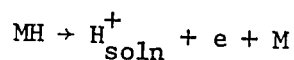
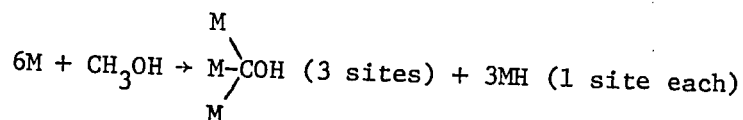
Two examples of reaction mechanisms, one for formic acid and the other for methanol oxidation, shown below, exemplify the

involvement of adsorbed intermediates in this class of reactions.

(a) formic acid oxidation:

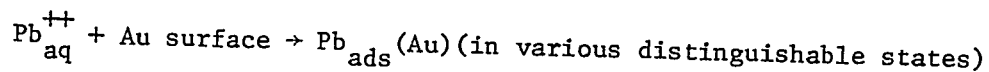


(b) methanol oxidation (represented as follows):



As can be seen, the carbon containing chemisorbed residue is oxidized by adsorbed OH particles in the rate-controlling step of the process.

Another example of a reaction mechanism, where adsorbed intermediates play an important role is the one in which underpotential deposition of metal atom on a substrate occurs from a metal ion in solution. A typical example is



At high cathodic potentials, bulk deposition of Pb crystals on the Pb atom layer occurs by a normal nucleation and growth mechanism. Underpotential deposition of Pb atoms in this example is analogous to that of H on Pt, Ir, Rh where an atomic monolayer is deposited, for example, prior to evolution of bulk H_2 at the thermodynamic reversible potential for the process $H^+ + e \rightleftharpoons 1/2 H_2$. Underpotential deposition of metal atom monolayers which can be regarded as a preliminary stage of overall metal crystal deposition arises when the metal-substrate bond energy in the monolayer is greater than the metal-to-metal bond energy in the bulk crystal which is subsequently formed on the monolayer.

The detailed study of adsorbed intermediates in processes such as those exemplified above is now an active area in experimental electrochemical surface science. However, since (a) various reaction sequences can be involved and (b) various types of adsorption behaviour of the ad-species can arise, it is necessary to make detailed kinetic analyses of various possible reaction schemes and states of adsorption from a theoretical point of view if the experimentally observed behaviour is to be at all well understood.

1.2 Dependence of Rates of Electrode Reactions on Electrode Metal - Solution Potential Difference

Reactions at electrode surfaces, since they involve a transfer of charge, are dependent on the metal-solution potential difference, $\Delta\phi$. The role of $\Delta\phi$ in equilibrium processes at electrode interfaces

is defined by the Nernst relation while in rate processes involving a net anodic or cathodic direction of reaction, $\Delta\phi$ modifies the free energy of activation according to the Tafel relation^{1,2} which in exponential form can be written in a general way as

$$i = zFk c_{A^{\pm}} \exp(\mp\beta\Delta\phi F/RT) \quad (1-1)$$

for a simple charge-transfer process



occurring at a net rate $i/zF \text{ mol s}^{-1} \text{ cm}^{-2}$ corresponding to a current-density, $i(\text{A cm}^{-2})$. β is a barrier symmetry parameter² corresponding to an electrochemical Brønsted factor³ and $\Delta\phi$ is taken negative for the cathodic direction of a reaction such as (1-2). In (1-1) and (1-2), the role of free electrode surface area, and either chemisorption of the product B or of a corresponding reaction intermediate, has not yet been specified. These important factors will, however, be dealt with in detail subsequently as they form the main basis of the subject matter of this thesis.

The kinetics of electrode reactions are normally studied either (a) by recording the influence of electrode potential (measured with respect to some reference electrode) on the reaction rate (controlled potential method) or (b) by measuring the changes of potential accompanying adjustment of the current-density to various values (controlled current method). Under steady-state conditions, these methods are referred to by the well-known terms "potentiostatic" and "galvanostatic", respectively. These methods apply to the study of

electrode reactions that can occur in a steady or continuous way, e.g. electrochemical evolution of gases such as H_2 , O_2 , Cl_2 , metal plating, anodic metal dissolution.

An important class of electrode reactions, however, involves only the deposition or dissolution of atoms at surfaces up to a coverage of a monolayer (or several layers) before some overall continuous reaction takes place. The study of such reactions cannot be made by steady-state techniques since only a small quantity of charge (e.g. ca. $220 \mu C \text{ cm}^{-2}$ for a monolayer of electrodeposited adsorbed H) is required to complete a monolayer. Thus, experimental methods required for studies of electrode "surface" reactions are necessarily of a transient or non-steady-state type so that the course of the reaction leading to deposition or dissolution of monolayer quantities of material can be followed. Such techniques require observation, on relatively short time scales, of either:

- (a) the time-dependence of currents resulting from a response to a changing potential ("potentiodynamic" or "potential-step" techniques); or
- (b) the time-dependence of potential resulting from passage of charge under controlled current conditions.

Method (a) has some experimental advantages over method (b) since the time-dependent potential function applied to the electrode can take several convenient and accurately controlled forms: (i) a potential-step () (ii) a linear potential-sweep () or a repetitive sweep () ["cyclic voltammetry"] and (iii) a sinusoidal

function ($\sim$ -alternating voltage). Method (a) is also, in some ways, a more fundamental technique since it is the "independent" variable $\Delta\phi$ that is modulated rather than the rate i/zF .

The linear or repetitive potential-sweep methods are especially useful for the study of electrode surface processes for reasons which will be discussed below.

1.3 Application of the Potentiodynamic Sweep Method to Studies of Adsorbed Intermediates and of Reaction Mechanisms at Electrode Surfaces

It is convenient first to classify electrode reactions into two main types:

(i) Simple redox reactions not involving chemisorbed intermediates, e.g. $\text{Fe}(\text{CN})_6^{3-} + e \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$ where the immediate product of an electron transfer step is a stable species in solution; and

(ii) More complex reactions where the electron transfer step is followed (or preceded) by some chemical step or a second electrochemical step, e.g. in the gas evolution reactions. As mentioned in Part 1.1, such reactions involve either

(a) an adsorbed intermediate

or

(b) a solution-soluble reactive intermediate as in a number of organic electrochemical reactions. Steps in the latter type of reaction are often diffusion-controlled.

In the last 20 years, the potentiodynamic sweep method has been frequently employed to study the kinetics and mechanisms of many anodic and/or cathodic electrochemical reactions. In this work, the method has been usefully applied to the study of diffusion-controlled simple and consecutive reactions of types (i) and (ii)(b) as well as to elucidation of the nature and the behaviour of intermediates formed in reactions of type (ii)(a).

In the latter type of reaction, it is quite common that one or more adsorbed intermediates are involved. The surface concentrations of such intermediates are in most cases potential dependent. The formation of a layer of intermediates requires passage of Faradaic charge in proportion to changes of coverage in the layer and is potential dependent; the charge involved can be experimentally measured with substantial accuracy.

Only in the case of diffusion-controlled reactions in which a simple redox step is involved⁴ or in cases where solution-soluble intermediates are produced⁵⁻⁷ have the results obtained by the potentiodynamic sweep method been quantitatively analyzed for selected cases. In the case of reactions involving chemisorbed intermediates, where application of the sweep method is especially convenient, the interpretation of the experimental behaviour leaves much to be desired especially in the case of consecutive surface reactions involving more than one adsorbed intermediate.

Here the application of the sweep method to diffusion-controlled reactions will first be reviewed briefly and then the previous

work on surface reactions involving chemisorbed intermediates will be examined in greater detail.

1.4 Diffusion-Controlled Processes

1.4.1 Processes without involvement of adsorption

Electrode processes can be diffusion-controlled when the rate-constants for the electron transfer and other steps (where applicable) are large and/or when reactant concentrations are small so that mass-transfer rates are comparable with reaction kinetic rates. In cases of multi-step reactions not involving chemisorption, diffusion of solution-soluble intermediates (e.g. radicals or radical ions) is an important aspect of the kinetics of diffusion-controlled electrode reactions.

The use of a voltage sweep method employing a periodic rapid linear change of potential with time ("oscillographic polarography") was developed first by Ševčík⁸ in the late 40's for study of diffusion-controlled processes occurring at mercury electrodes. In his paper he derived exact mathematical equations for such reaction conditions and compared the predictions of these equations with experimental results. The difference between "diffusion-controlled" and "kinetically-controlled" currents, which can be easily distinguished, was stressed and fully discussed.

The mathematical expressions for more complex reactions, where a chemical reaction step was assumed to precede, to follow or to

catalyze a reversible or irreversible charge-transfer step with which it was coupled, were developed by Nicholson and Shain^{5,6} and Nicholson⁷. The detection of solution-soluble electroactive intermediates was also discussed^{9,10}. A numerical method was developed by Nicholson and Shain^{5,6} to solve the partial differential equations with the appropriate boundary conditions for each reaction mechanism considered, and thus they were able to compute theoretical current-potential profiles for each case under different "experimental" conditions. Comparison of the theoretically predicted behaviour with that observed for given experimental systems made it possible^{5,6} to determine the reaction mechanism through a set of diagnostic criteria which the authors developed, such as changes in peak currents, i_p , half-widths potentials, $\Delta V_{1/2}$, and the ratio of anodic to cathodic peak currents as a function of sweep-rate. Their mathematical approach consisted of solution of the boundary value problem, which arises in any case of diffusion at a boundary plane, by means of an integral equation discussed elsewhere¹¹⁻¹³, rather than by using the Laplace transform technique⁸ which is feasible only for the simplest cases.

Theoretical calculations similar to those of Nicholson and Shain^{5,6} were reported by Savéant and Vianello^{14,15} a few years later; they derived general diagnostic criteria for any type of chemical reaction (not just first-order) which accompanies a single electron transfer. Determination of rate constants of the chemical reactions in question from polarization curves was discussed as well. Theoretical current-potential curves for all the cases considered were calculated.

This section is concluded by a tabular summary of other work on diffusion-controlled processes studied by the linear potential sweep method and other perturbation techniques (see following page).

1.4.2 Coupled diffusion and adsorption processes

Important cases arise when either the reactant, the product or both, are adsorbed on the electrode, so that surface reactions coupled with diffusional mass-transport and reaction, occur. The theory of stationary electrode polarography for cyclic voltammetry conditions has been extended in a number of papers²⁵⁻²⁸ to these cases, where a species may be adsorbed on the electrode. Correlation of the theoretical with the experimental parameters makes it possible to develop diagnostic criteria for the reaction kinetic behaviour expected under various conditions so that an unknown system can be kinetically characterized by studying the variation of the current-peak shapes and peak currents as a function of sweep-rate and bulk reactant concentration. For example, in the presence of a weakly adsorbed species, the polarograms exhibit an increase of peak currents relative to those for absence of adsorption. If, however, the material is strongly adsorbed, a separate adsorption peak may occur just before or just after the normal peak for the electron-transfer reaction. Such peaks are called "pre-peaks" and "post-peaks", respectively, and originate because Faradaic currents can arise from the adsorbed layer of reactant as well as from reactant transported in the diffusion-layer from the bulk solution.

TABLE 1-1

Summary of Other Recent Theoretical Work on Diffusion-
Controlled Processes under Linear Potential-Sweep Control

Author	Description	Ref. No.
D.H. Evans see also M.L. Olmstead et al.	Completely reversible heterogeneous electron-transfer reaction followed by an irreversible chemical reaction, which can be either first or second order.	16 see also 17
K. Kontturi et al.	Kinetics of diffusion-controlled processes such as e, e.c. and catalytic reactions were solved analytically using nonlinear perturbation functions.	18
Ruziĉ and Feldberg	Previously developed techniques ^{19,20} were applied to diffusion phenomena at the growing mercury drop electrode, assuming that the mercury drop is a perfect sphere.	21
Grennes and Oldham see also Oldham and Spanier, and Oldham	The technique of semi-integral analysis was developed for diffusion processes and verification of this theory in relation to appropriate experimental results was discussed.	22 see also 23 and 24

Wopshall and Shain^{25,26} derived equations and theoretical current-potential profiles for such adsorption and diffusion processes, where currents from an adsorption layer at the electrode surface are included. In the simplest cases, Langmuir type isotherm behaviour is considered (e.g.^{29,30}) for the various adsorbed species but more complex isotherms are usually required to represent the adsorption realistically³¹⁻³⁴. In the work of Wopshall and Shain, the integral equation method^{5,6,11-13} was again used to solve the boundary value problems. All possible combinations of either weak or strong adsorption of reactants and products were considered and diagnostic criteria determined for each case. Various experimental cases were also considered^{26,35}.

One of the most thorough mathematical treatments of diffusion processes was given by Feldberg¹⁹ who developed elaborate computer programmes for different types of reaction mechanisms. He pointed out that analytical mathematical expressions relating all the important terms, such as current, potential, time, concentrations of reactant and product and kinetic parameters are very difficult, if not impossible, to obtain and evaluate. It was for this reason that he developed a comprehensive computer programme for the main types of reaction sequence. The programming language employed was "FORTRAN" and the required integrations were performed by the well-known method of finite differences³⁶⁻³⁹. This treatment was developed further by Feldberg²⁰ who discussed in detail diffusion processes involving multiple electron transfers and adsorption of either reactant or product, or

both, occurring simultaneously²⁰. Current-potential curves for representative cases together with those for adsorption according to Langmuir or Temkin type isotherms, where applicable, were shown and general criteria governing such reactions were discussed.

It is to be noted that pure "surface" processes, (viz. deposition and dissolution of monolayer quantities of species at electrode interfaces) which form the main topic of the original calculations to be presented later in this thesis, are rarely diffusion-controlled except at rather low reactant concentrations because the quantity of material required to form a monolayer is always very small, ca. $\leq 10^{15}$ atoms cm^{-2} or $\approx 1.66 \times 10^{-9}$ mol cm^{-2} . Thus, in a 1 M solution, this quantity of chemically reactive material can be supplied by 10^{-6} cm^3 of solution, i.e. per cm^2 from an $100 \text{ \AA}$ lamina of solution near the electrode interface. The mean diffusional transport time from such a lamina is of the order of a mere 0.1 μs .

1.5 Electrochemical Surface Processes Involving Monolayer Formation and Dissolution

Much of the most interesting recent work in electrochemical surface science has involved study of the deposition and dissolution of monolayers of species such as H, metal atoms, and OH and O species at noble metals. The species involved are often, in a formal chemical sense (though not necessarily in a kinetic mechanistic sense), intermediates in some overall multistep electrode reaction, e.g. H_2 , O_2 evolution or in the case of metal atoms, metal crystal phase formation as has been described in Part 1.1.

If these types of processes are compared with diffusion-controlled ones, the principal difference is that the concentrations of reactants and/or products at the electrode surface do not significantly change, as has been stressed above, and are usually identical with concentrations of the same species in the bulk solution. From the mathematical point of view of simulating the kinetic behaviour of such reactions, e.g. its current-potential profiles as a function of sweep-rate under potentiodynamic sweep control, the calculations are radically simplified when it can be assumed that diffusion of the soluble electroactive reactant species does not limit the rate of the surface reaction to be studied.

1.5.1 Studies of adsorbed intermediates

As has been mentioned earlier, many electrochemical reactions occur in more than one step, thus giving rise to adsorbed intermediates which then undergo further chemical or electrochemical reactions to produce a final, stable product. In most electrochemical processes where adsorbed intermediates are formed, the potential plays a characteristically important role in addition to the reactant concentration and temperature in determining the surface coverage of an intermediate.

1.5.1.1 Langmuir isotherm and adsorption at electrodes

In the simplest case corresponding to the Langmuir isotherm:

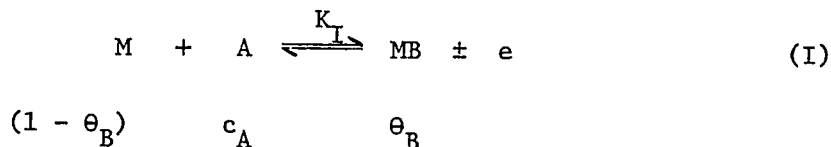
- (a) The free energy of adsorption of the species is potential-dependent and, as a consequence;

(b) The coverage of the species in going from a bare substrate surface to one with full monolayer coverage, is potential dependent in a well-defined manner.

Also

(c) The free energy of the adsorbed layer depends only on some configurational function of sites occupied, i.e. fractional coverage θ , and does not involve lateral interaction effects, i.e. K_I below is a true thermodynamic equilibrium constant, independent of the value of coverage.

In these cases, the electrochemical adsorption of a species B arising from a reactant A in solution according to a process such as



where A is a charged species, is determined by an electrochemical adsorption isotherm of the Langmuir form:

$$\frac{\theta_B}{1 - \theta_B} = K_I c_A \exp\left(\frac{\Delta VF}{RT}\right) \quad (1-3)$$

where ΔV is the difference of electrode potential at any θ_B from the standard potential³⁰ corresponding to $\theta_B = 0.5$, and K_I is the chemical equilibrium constant for surface reaction (I) related to the standard free energy ΔG_I° of reaction (I). Other symbols in eqn. (1-3) have their usual significance. Langmuir adsorption conditions are defined by independence of K_I on coverage, θ_B . In practice, this is not

usually the case, as will be treated in more detail subsequently. The statistical-mechanical basis for the Langmuir isotherm is well-known⁴⁰ and serves to define its limitations.

1.5.1.2 Temkin isotherm

In many cases of real systems, condition (c) in Section 1.5.1.1 no longer obtains because K_I depends on coverage on account of (a) lateral interactions and/or (b) variation of the standard free energy of adsorption with coverage due to intrinsic heterogeneity of the surface.

The quantitative treatment of factor (b) above was given by Temkin who based his treatment of adsorption on experimental evidence, taken both from gas-phase adsorption studies and from electrochemical kinetics, that chemisorption energies often varied linearly with coverage. Temkin proposed a model in which the surface was regarded as being made up of a distribution of small patches, with adsorption on each being characterized by a Langmuir isotherm but with an independent and progressively changing K_I value. It was shown experimentally that the heat of adsorption, ΔH_{ads} , usually decreases numerically with increase of coverage, θ . The relation between ΔH_{ads} and θ was shown to be approximately linear at intermediate values of θ (i.e. $0.2 < \theta < 0.8$). It is therefore possible to write an equation for the standard free energy, which decreases linearly with increasing surface coverage θ , as follows:

$$\Delta G_{\theta}^{\circ} = \Delta G_{\theta=0}^{\circ} + gRT\theta \quad (1-4)^{*}$$

Although the "g" parameter in Temkin's isotherm is associated with intrinsic heterogeneity of the surface, a similar relation arises empirically in Frumkin's adsorption equation³⁴ and from the induced heterogeneity model of Boudart⁴¹ based on electronic interaction effects at the adsorbate/adsorbent interface.

The Temkin adsorption isotherm can be written for an electrochemical process of type (I) under equilibrium conditions in the following form [cf. eqn. (1-3)]:

$$\frac{\theta_B}{1-\theta_B} = K_I c_A \exp\left(\frac{\Delta VF}{RT}\right) \exp(-g\theta_B) \quad (1-5)$$

At intermediate values of coverage and for sufficiently large g, i.e. when the term $\frac{\theta_B}{1-\theta_B} \approx 1$ and its variation with θ_B is small compared with that of the $\exp(-g\theta_B)$ term, the equation (1-5) can be reduced to

$$\exp(g\theta_B) \doteq K_I c_A \exp\left(\frac{\Delta VF}{RT}\right) \quad (1-6)$$

which upon rearrangement gives

$$\theta_B = \frac{1}{g} \cdot \frac{\Delta VF}{RT} + \frac{1}{g} \ln (K_I c_A) \quad (1-7)$$

* The direction of the effect of the $gRT\theta$ term in this equation is such as to make the apparent standard free energy of adsorption $\Delta G_{\theta}^{\circ}$ less negative or more positive with increasing θ if there are lateral repulsion effects in the ad-layer, i.e. for g taken positive. In the case of interaction effects, g is related to the activity coefficient for species in the ad-layer in terms of coverage θ . In the case of intrinsic heterogeneity, g is an empirical parameter which measures the distribution of adsorption energies as a function of sites occupied over the intermediate coverage range $0.2 < \theta < 0.8$, approximately.

Hence for constant K_I and c_A values, the coverage tends to increase linearly with increasing potential difference ΔV (contrast the Langmuir case of low θ_B where θ_B tends to increase exponentially with ΔV) and increases logarithmically with increasing K_I or c_A values at constant potential difference ΔV (cf. rearranged eqn. (1-3) for the case of the Langmuir isotherm). Although Temkin's isotherm has been applied to the behaviour of many electrode processes, it should be noted that in recent years it has been found (in fact by the potentiodynamic sweep method) that chemisorption at electrodes often occurs in a range of discrete states with different binding energies rather than with a continuous range of energies of adsorption.

From an electrochemical point of view, an important feature of equation (1-3) or (1-5) relating θ_B to ΔV is that a characteristic equilibrium value of θ_B between 0 and 1 exists for every value of potential as the adsorbed layer is deposited or removed, provided that the kinetics of the deposition or desorption process are such that electrochemical equilibrium is maintained. Cases where the equilibrium is disturbed when the deposition or desorption process is driven fast will be considered subsequently.

There are three important and distinct reasons for the decrease of heats of adsorption with increasing surface coverage, which have been recognized for electrosorption as well as gas-solid adsorption:

- (a) a priori heterogeneity, e.g. due to polycrystallinity, occurrence of edges, (steps), kinks, grain boundaries,

etc., in the surface;

- (b) induced heterogeneity⁴¹ (or work function effect);
- (c) mutual interactions of adsorbed species, e.g., due to surface dipole-dipole repulsions or electronic effects.

A priori heterogeneity is inevitably present in all polycrystalline metal surfaces used as electrodes and, even on single-crystal planes, some residual steps and kinks in steps, as well as thermal defects at finite temperature, will be present.

If the adsorbed species is immobile, heterogeneity will not be detectable by observation of a coverage-dependent heat of adsorption, since sites of varying energy will be filled at random and the measured heat of adsorption will be an average value. For the initial stages of mobile adsorption, on the other hand, the particles will preferentially tend to populate regions of highest adsorption energy at a heterogeneous surface and, in this case, local lateral interactions may then be significant as well and themselves depend on the heterogeneity effects.

A second cause of the fall in heats of adsorption with increasing coverage has its origin in the corresponding progressive change in the work function of the surface. The relevant theory was originally developed by de Boer⁴² to interpret the fall in (exothermic) heats of chemisorption with coverage. Boudart⁴¹ developed another approach which may be called the "dipole double-layer model" in which the decrease in heat of adsorption with increasing coverage was

related to changes in the electronic work function ϕ of the metal due to adsorption. There is good evidence that the change in the free energy of adsorption is proportional to the change of ϕ due to chemisorption and thus a linear variation of the heat of adsorption with coverage is predicted as an approximation (dipole depolarization at high θ causes deviations from linearity).

The third main cause of the fall in heats of adsorption with increasing coverage arises from mutual interactions of the adsorbed species (surface dipole-dipole and van der Waals forces). When surface diffusion is possible, the particles will distribute themselves at optimum distances on a homogeneous surface and the interaction energy at a given coverage will be an average value determined by θ .

If the decrease in the apparent standard free energy of adsorption were attributed to nearest neighbour ion-ion or dipole-dipole repulsions alone, the apparent standard free energy of adsorption should fall off linearly with $\theta^{1/2}$ or $\theta^{3/2}$, respectively, rather than with θ . It should be remembered that the $\theta^{1/2}$ and $\theta^{3/2}$ relationships can only arise if the discreteness of surface sites is not considered, i.e., if it is assumed that the distance r , between ions or dipoles on the surface can vary continuously with θ . Moreover, an adsorbed layer of ions is probably associated with image charges, thus leading fundamentally to a dipole-dipole type of interaction, as well. It can be shown that such interactions on a set of discrete adsorption sites lead to an interaction term proportional to θ and,

hence, to a linear fall of the free energy of adsorption with increasing θ .

If a distribution of heats of adsorption is introduced, this can also lead to falling of $-\Delta H_{\text{ads}}$ with coverage, if the film is mobile, then a Freundlich-type isotherm results. It is, however, beyond the scope of this thesis to consider this type of isotherm while other types, such as the BET, are not relevant. Further discussion of these isotherms may be found in standard texts, e.g.,^{43,44} and in a recent review⁴⁵.

1.5.1.3 Methods for determination of coverages of both electroactive and electroinactive adsorbed species at electrodes

As mentioned earlier, the behaviour of intermediates in electrochemical reactions was always of interest to electrochemists even before the voltage sweep method became widely used as a tool for such studies. It is useful to review briefly some other frequently used methods to study the behaviour of chemisorbed species at electrodes.

In studying adsorbed species at electrodes, it is necessary to distinguish whether the particular species is electroactive, i.e., easily participates in a charge-transfer reaction such as (I) (p.17) or electroinactive. The methods for electroactive intermediates will be discussed first and are based on direct observations of electrical effects which are associated with changes of coverage on the electrode.

(a) Galvanostatic "charging"

In this method the electrode is first maintained at a constant potential* at which the coverage of the electrode is to be determined. When equilibrium at this potential is attained, the electrode is then subjected to a constant current pulse and the resulting potential-time transient is recorded. This method was first used by Bowden and Rideal⁴⁶ who studied the capacity of the double-layer in this way. Later this method was used by other workers for studying hydrogen adsorption⁴⁷⁻⁵⁰ and for oxygen coverage at electrodes^{51,52}.

(b) Potentiostatic step method

In this method, a rapid change of potential is applied to the electrode, usually from a potentiostat and the resulting time-dependent "relaxation" current is recorded. This is the current associated with changing the coverage of the electrode by whatever electro-active species can be generated or desorbed over the potential range of the applied potential step. The corresponding charge required to oxidize or reduce the adsorbed species is simply the area ($\int i dt$) under the recorded transient current-time curve.

(c) Other methods used less frequently

These methods include:

- (i) recording of open-circuit potential decay curves;

*The potential must be one at which no overall evolution of an electroactive molecular product, e.g., O_2 , H_2 , Cl_2 is occurring.

(ii) recording of coulstatic or charge-step potential transients, and

(iii) a.c. bridge methods where the electrode capacitance is measured as a function of potential⁵³⁻⁵⁵.

Detailed descriptions of these methods are given elsewhere, e.g.,⁵⁶⁻⁵⁸.

(d) Linear voltage sweep method

This technique will be discussed in more detail separately later in Section 1.5.1.4 as the analysis for this method forms the main basis of the original work reported in this thesis.

The second class of adsorbed species often encountered in electrode reactions are electro-inactive intermediates, i.e., those that are not themselves directly deposited on or desorbed from the electrode surface in an electron transfer step. A widely used method for studying intermediates of this kind is to employ any of the methods detailed above, first in the absence and then in the presence of the given electro-inactive component. The extent of its coverage may then be deduced indirectly by considering: (i) the extent of blocking of hydrogen adsorption sites which the electro-inactive species occupy as compared to the extent of hydrogen adsorption when such (usually organic) species are absent, (ii) the charge required for oxidative desorption of the intermediate, e.g., at a Pt electrode, as compared to the oxidation charge for the metal surface itself when the chemisorbed organic species are absent.

1.5.1.4 Voltage sweep method applied to studies of adsorbed intermediates

The linear voltage sweep method is now one of the most widely used techniques for studying electrochemical reactions involving either adsorbed electro-active or electro-inactive intermediates. The potential is usually varied linearly with time at some known rate and the current is recorded as a function of potential. If the sweep-rate is changed periodically in sign, so that the V-t relation is triangular, the method is referred to as cyclic voltammetry. Experimentally, the sweep-rate can be varied from about 1 mV sec⁻¹ or less up to several hundred V sec⁻¹.

The basis of the method is as follows: currents for an electrode surface process such as $M + A \rightarrow MB \pm e$ (reaction (I), p.17) when occurring anodically are represented by the equations

$$\vec{i} = zFk_1(1-\theta_B)c_A \exp(\beta\Delta\phi F/RT) \quad (1-8)$$

and

$$\overleftarrow{i} = zFk_{-1}\theta_B \exp(-(1-\beta)\Delta\phi F/RT) \quad (1-9)$$

for the back reaction of (I), where $\Delta\phi$ is the metal/solution potential difference and β ($\approx 1/2$) is a Brønsted or energy barrier symmetry factor for the charge-transfer process. The net current $i = \vec{i} - \overleftarrow{i}$ or $i = \overleftarrow{i} - \vec{i}$ is measured as a function of the time-dependent $\Delta\phi$ in the potential sweep. For a surface process such as deposition or desorption of B, to or from a monolayer limit, $\vec{i}$ or $\overleftarrow{i}$ are not continuous and can only be observed by some transient technique; thus, (Fig. 1-1) $\vec{i} \rightarrow 0$ as

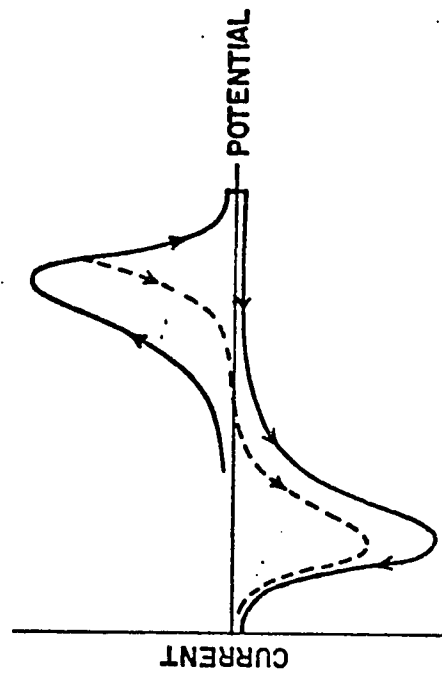
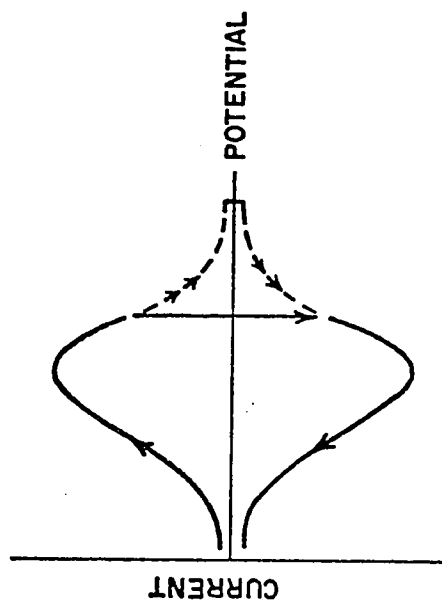


Fig. 1-1 Schematic representation of differences between current-potential profiles for a continuous Faradaic reaction and a 1-e electrochemical surface process which can behave either reversibly or irreversibly.

$\theta_B \rightarrow 1$ and $i \rightarrow 0$ as $\theta_B \rightarrow 0$ and $\Delta\phi$ is small. Generally, i or i is a function of potential V in the sweep as V is varied linearly with time at a sweep-rate $s = dV/dt$. The time-dependent current i or i or their difference is denoted as i . Then coverage θ_B attained at any potential in the sweep is

$$\theta_B = \int \frac{idt}{Q} \quad (1-10)$$

where Q is the charge for forming a monolayer of B . Introducing $s = dV/dt$ for the sweep experiment enables eqn. (1-10) to be rewritten as

$$\theta_B = \int \frac{idV}{Qs} \text{ (for adsorption) or } \theta_B = \theta_{B,in} - \int \frac{idV}{Qs} \text{ (for desorption) } \quad (1-11)$$

Coverages are hence evaluated from the integral of the i - V profile generated by application of the potential-sweep to the electrode where $V = V_{in} \pm st$ where V_{in} is the initial potential in the sweep.

Alternatively, since $i = dq/dt$ in general, where dq is the element of charge passed by the current i in time dt , i can be written

$$i = \frac{dq}{dt} \equiv \frac{dq}{dV} \frac{dV}{dt} \equiv \frac{dq}{dV} s \quad (1-12)$$

dq/dV has the nature of a capacitance associated with the electrode process, C_{Tot} , i.e., $i = C_{Tot}s$. C_{Tot} is made up of a double-layer charging component and a component arising from the potential-dependence of coverage θ_B of the surface by B . The latter is the so-called adsorption pseudo-capacitance for B , $C = dq_B/dV$. Thus, $C_{Tot} = C_{d.l.} + C$. Since θ_B and q_B are related by $\theta_B = q_B/Q$ for any coverage ≤ 1 , i is a

linear* function of s as follows:

$$i = C_{d.l.} s + Q \left(\frac{d\theta_B}{dV} \right) s = C_{d.l.} s + C s \quad (1-13)$$

An important feature of the potentiodynamic method is that the profile of i with changing potential at the rate s ($=dV/dt$) hence gives directly $d\theta_B/dV$ which is the differential coefficient of the electrochemical isotherm for adsorption of A in the process (I). The double-layer charging contribution $C_{d.l.} s$ in eqn. (1-12) can usually be subtracted from i by calculation or from other experimental data.

It should be mentioned that in a number of cyclic-voltammetry experiments, the interpretation of results is often more complicated than for (I) because currents for both the overall Faradaic reaction and for surface charging processes occur over the same potential range; also, reaction mechanisms occurring at electrode surfaces are often by no means as simple as (I). The advantages which this method has lie in the possibility of accurate and rapid measurement of the behaviour of complex reactions at electrode surfaces. An important limitation of the potential sweep method applied to the study of surface processes has hitherto been that quantitative interpretations of experimental results have been difficult to make because the method has lacked a rigorous theoretical treatment for non-diffusion-controlled surface processes in the non-steady state (see Section 1.5.2), especially for cases of sequential surface reactions which are often of greatest interest experimentally.

* Pure surface processes are distinguished by this relation from diffusion-controlled ones for which currents are proportional to $s^{1/2}$.

It is the aim of work to be described in this thesis to show how at least a number of relatively simple surface reactions can be investigated by this method and the results interpreted quantitatively. Also a number of general kinetic criteria for distinguishing various types of surface processes can be derived, as will be discussed in later chapters.

1.5.1.5 Experimental studies of some systems using the potentiodynamic method and interpretation of the results

The potential sweep method was first applied to non-diffusion controlled surface processes by Will and Knorr⁵⁹ in the early 60's. This method was experimentally elegant and rapid, and enabled information to be obtained on processes involving electrochemical adsorption and desorption of chemisorbed species at electrode interfaces. In most cases, the application of this technique has evolved around studies of hydrogen and oxygen sub-monolayer films on the noble metals, especially Pt. More recently it has been applied to the study of metal atom monolayers and chemisorbed organic molecules⁶⁰⁻⁶².

Will and Knorr⁵⁹ described the principles and applications of the triangular voltage sweep method and gave experimental results on formation and removal of adsorbed hydrogen and oxygen layers on platinum electrodes. They concluded that hydrogen is adsorbed and desorbed reversibly, except at high sweep rates ($s \geq 50 \text{ V sec}^{-1}$), whereas oxygen deposition and removal always occurs irreversibly.

Similar conclusions also follow from much earlier work^{47-49,63} using galvanostatic charging.

(i) Hydrogen adsorption

The general features of H adsorption and desorption behaviour on Pt electrodes are as follows:

(a) the species is adsorbed and desorbed from the electrode reversibly except at high sweep rates, where irreversible behaviour sets in;

(b) the multiplicity of peaks observed in the current-potential profiles cannot be attributed to adsorption of hydrogen on to sites of intrinsically different adsorption energies, since multiplicity is maintained on well prepared single-crystals⁶⁴;

(c) the peaks in the i-V profiles cannot be the result of some follow-up electrochemical reaction, because no such reaction involving formation and removal of adsorbed H can be envisaged and no diffusion process is significant, e.g., into the lattice, as at Pd.

(ii) Adsorption of oxygen species

The nature and extent of adsorption of oxygen species at Pt, and the mechanisms of oxide formation and reduction, are much more complicated than those for adsorption of H. The features of the behaviour of oxygen species at Pt are:

(a) the overall i-V profile for an anodic followed by a cathodic-going sweep is characteristic of an irreversible process;

(b) the initial stages of oxidation of Pt and other noble metals involve an almost reversible stage of OH electrosorption;

(c) the OH species deposited below a monolayer take up various geometrical sub-lattice arrangements on the surface;

(d) as more and more OH species become adsorbed, the current-potential profiles start to show features corresponding to an irreversible process, even below the potential where higher oxides can be formed;

(e) it can therefore be concluded that some kind of chemical transformation, which gives rise to hysteresis, must be occurring;

(f) a place-exchange type of mechanism, such as that proposed by Lanyon and Trapnell⁶⁵ for oxygen adsorption on noble metals, seems to be the best explanation for the observed hysteresis.

Electrochemical formation and reduction of surface oxides on platinum has been studied recently using both the linear sweep voltammetry⁶⁶, and optical and impedance techniques⁶⁷. The new experimental results^{66,67} confirm the general conclusions mentioned above.

(iii) Chemisorption of organic species at electrodes

In electrocatalytic reactions, co-adsorption of organic intermediates (which may be either electro-active or inactive) with OH, O or H species may often arise. Then the current-potential profiles in potentiodynamic studies may change drastically from those associated with reactivity of OH, O and H depending on the organic species present in the electrolyte. These differences enable⁶⁸⁻⁷³ quantitative information to be derived on the state and coverage by chemisorbed organic species at noble metal electrodes.

Electrosorption effects which arise when electro-active nitriles are chemisorbed at platinum electrodes in the "double-layer" and "hydrogen" potential regions have been studied by MacDougall et al.⁶⁰ and Angerstein-Kozłowska et al.⁶¹ in this laboratory. Cyclic voltammetry experiments over the hydrogen region in the presence of chemisorbed acetonitrile showed that hydrogen chemisorption is substantially, but not completely, blocked by the adsorbed acetonitrile. CH_3CN is found to be reactive in the chemisorbed state but no solution-soluble species are generated in cyclic voltammetry.

Kinetic and optical relaxation techniques using the potentiodynamic sweep method, with faster sweep modulation were treated by Conway et al.⁷⁴. They described a relaxation method, which is useful for distinguishing processes where two different electrochemisorbed species, electro-active over the same potential range, are involved. Theoretical simulations of this situation, described later in this thesis (Chapter V), were made and reported in ref. 74.

Studies of adsorption effects for non-diffusion-controlled conditions in polarography were made by Laviron and Riollot⁷⁵, Laviron^{76,77}, and by Laviron and Vallat⁷⁸. The systems were studied experimentally both by classical polarography and cyclic voltammetry. The results obtained from the two techniques were compared and treated in terms of theoretical calculations (to be discussed in Sections 1.5.2.1 and 1.5.2.2) which Laviron developed in other papers⁷⁹⁻⁸⁷.

1.5.2 Kinetic studies of various reaction mechanisms by the potential-sweep method

1.5.2.1 Theoretical treatments of a simple 1-electron electrochemical reaction

The first theoretical treatment for an electrochemical surface reaction was made by Eucken and Weblus⁸⁸ for transients in H deposition and by Bockris and Kita⁸⁸ for metal deposition. Conway and Gileadi^{31,32,89} gave a detailed treatment for 1-e surface processes at equilibrium where adsorbed species obeyed a Langmuir or Temkin type isotherm. In this work, an attempt was made to establish both qualitatively and quantitatively a set of diagnostic criteria which characterize the behaviour of the 1-e surface reaction. Although no current-potential or pseudocapacitance-potential curves were simulated for the potentiodynamic sweep method, most of the diagnostic criteria for a quasi-reversible 1-electron electrochemical surface reaction for both Langmuir and Temkin types of isotherm were derived. The diagnostic parameters, which were determined in a series of papers^{31,32,89} include values for maximum current, i_p , maximum capacitance, C_p , potential at the maximum current, V_p , coverage of the adsorbed electro-active species at the maximum current, θ_p , and the width of the potential V_f at a given fraction f of the maximum value of capacitance C_p . Usually $f = 0.5$ is taken and this width is then called the "half-width potential", $\Delta V_{1/2}$. Although Conway and Gileadi did not simulate the current-potential curves directly from the differential equations for the rates of the 1-e electrochemical reaction, they performed the evaluations³¹ at various potentials and

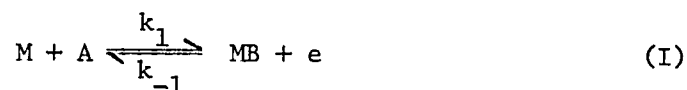
thus derived the adsorption pseudocapacitance as a function of potential and θ for different g values in the isotherm [eqn. (1-5)] for equilibrium electrochemical adsorption conditions.

The conclusions of the theoretical calculations were applied to various reactions, e.g., oxygen evolution³¹ and H-recombination at Pt³¹.

In a further development of this work, Gileadi and Conway^{32,89} derived the pseudocapacitance-potential/and-coverage, relations for an electrochemical adsorption process coupled to a following desorption step under steady-state, in distinction to quasi-equilibrium, conditions. The electrochemical adsorption behaviour was derived for various degrees of displacement of the equilibrium in the electro-sorption step and characteristic relations were obtained for the following reaction mechanisms:

- (i) discharge followed by atom-atom recombination⁸⁹;
- (ii) discharge followed by ion-atom desorption^{32,89};
- (iii) discharge followed by first-order decomposition⁸⁹.

It was not until 1966, in a paper by Srinivasan and Gileadi⁹⁰, that the behaviour of the 1-e surface reaction (I)



(treated in the earlier papers for equilibrium and steady-state conditions) under linear potential sweep control was theoretically analyzed, They considered three cases which can arise in reaction (I):

(a) complete equilibrium; (b) total irreversibility (back reaction neglected) and (c) a general case of quasi-equilibrium where the forward and backward rates are comparable but not equal, so that the backward reaction cannot be neglected.

For cases (a) and (b), expressions for all the important diagnostic parameters were derived analytically, e.g., for peak current, i_p , peak potential, V_p , and coverage at the current peak, θ_p . For case (c) analytical solutions to the problem cannot be obtained.

The main kinetic features of the 1-e reaction (I) under linear potential sweep conditions were derived in this work and the transition from equilibrium to complete irreversibility in the electro-sorption reaction was evaluated in terms of the form of i - V profiles for various sweep rates.

The authors used the following equation to express the current as a function of changing potential for reaction (I).

$$i = Q[k_1(1-\theta_B) \exp(\frac{\beta VF}{RT}) - k_{-1} \theta_B \exp(-\frac{(1-\beta)VF}{RT})] \quad (1-14)$$

where k_1 and k_{-1} are the forward and reverse specific rate constants and θ_B is the fractional surface coverage by adsorbed species B. Since the potential is varied linearly in time such that

$$\frac{dV}{dt} = s = \text{constant} \quad (1-15)$$

it is therefore possible to write

$$V = V_{in} + st. \quad (1-16)$$

If it is assumed that $\beta = 0.5$, then eqn. (1-14) can be simplified to

$$i = Q[k_1(1-\theta_B) \exp(\frac{V}{b}) - k_{-1}\theta_B \exp(-\frac{V}{b})] \quad (1-17)$$

where

$$b = \frac{RT}{\beta F} = \frac{2RT}{F} \quad (1-18)$$

By examining the behaviour over a range of sweep-rates and taking appropriate values for the rate constants k_1 and k_{-1} , Srinivasan and Gileadi⁹⁰ were able to generate a family of pseudocapacitance-potential curves (C-V) such that all three reaction conditions could be recognized, i.e., for equilibrium, quasi-equilibrium and irreversible behaviour. In their treatment of the 1-e surface reaction, Srinivasan and Gileadi limited their calculations to the case of $g=0$ (no interactions-Langmuir case).

The most important part of their work was case (c) where it was demonstrated that simply on account of change of sweep-rate it is possible to obtain simulated curves for quasi-reversible and irreversible conditions as well as for the transition from reversibility to irreversibility in the reaction. The important conclusions were (a) that the sweep-rate range where the change from complete reversibility to complete irreversibility occurs is indicated by a change of shape of the i-V profile; and (b) that the i-V profiles depend not only on the sweep-rate, but rather on the ratio s/k_1 where k_1 is the rate constant of (I). It is this ratio which indicates in what range of values s must be in relation to k_1 in order to be able to distinguish all three regions (reversible, intermediate and irreversible) as the

sweep-rate is changed and to observe the characteristic change of peak shape and position.

In the plot of V_p versus $\log s$, the position of the curve was shown⁹⁰ to depend on the values of both k_1 and k_{-1} . It is possible, however, for the curves to be normalized noting that the values of k_1 and k_{-1} contain an exp. term involving E° , the standard potential for the surface process³⁰. It would then have been possible to have drawn a single master curve, in terms of a normalized and reduced variable, that would be independent of k_1 , k_{-1} and E° values. This will be shown in Chapter IV; a similar treatment was given by Laviron^{79,80,85-87}, for this generalized case.

Srinivasan and Gileadi concluded that the theoretical analysis of potentiodynamic sweep method could be extended to cases where the apparent standard free energy of adsorption varies with coverage [i.e., $g \neq 0$ in eqn. (1-4)] corresponding to Temkin type adsorption. They claimed that for such conditions only numerical solutions could be obtained. This is true for the simulation of C-V profiles, but it will be shown in Chapter IV that the characteristic parameters i_p , V_p , θ_p and $\Delta V_{1/2}$ may in fact be derived analytically for both reversible and irreversible conditions.

A general treatment for the derivation of capacitance-potential curves for the 1-e surface reaction when the activation energy is assumed to vary with coverage, θ_p , was given by Hale and Greef⁹¹. Rather than the convenient Temkin case where the activation energy $E^\ddagger$ for the deposition process is regarded as changing linearly with

coverage θ_B , they proposed an arbitrary function where $E^\ddagger$ is represented as a power series in coverage. Using this type of function they solved the differential equation for reaction (I) analytically for both reversible and irreversible conditions and applied the results to the case of behaviour of adsorbed hydrogen on noble metals.

Experimentally, two principal peaks are observed under certain conditions (actually in dilute acid solutions four peaks can be experimentally resolved, e.g., on Pt⁶⁴). Then with only one charge transfer reaction with adsorption they were able to simulate C-V profiles having two peaks, simply because the interaction parameter was described in terms of a polynomial in integral powers of θ . A Taylor series polynomial of the third degree was taken having the following form:

$$f(\theta) = a_1\theta + \frac{a_2\theta^2}{2!} + \frac{a_3\theta^3}{3!} \quad (1-19)$$

Depending on the parameters a_1 , a_2 and a_3 they were able to produce C-V profiles having two peaks, the separation and height of which depended on the particular set of the parameters chosen, as shown in Fig. 2 of ref. 91. It seems, however, improbable that the four well resolved hydrogen peaks which are observed at noble metals would correspond to just one electrochemical reaction (i.e., with a single-valued standard free energy of adsorption) for which high orders of interactions would be required to account for the multiple peaks. It is more realistic to presume that multiple peaks for hydrogen adsorption originate because there are different energy states available on the

metal surface or because different states are generated, e.g., by d-orbital splitting, as the surface is progressively occupied up to $\theta_H \rightarrow 1$.

Stonehart, Conway and Kozłowska⁹² reviewed the problem of solving the kinetic equations for electrochemical surface processes under linear potential-sweep conditions and extended the calculations of Srinivasan and Gileadi⁹⁰ to include not only the interaction parameter g arising from heterogeneity and/or interaction effects of adsorbed species, but also cases where reaction orders for the surface process differing from unity could arise. The various cases can be distinguished by examination of the half-widths of i - V profiles, the dependence of the i - V profiles on sweep-rate and the effect of sweep-rate on the peak-current and the peak-potential V_p .

It was found that symmetry of the cathodic i - V profiles for oxide film reduction at Pt depend on quantity of the surface oxide being reduced. The possibility that the asymmetry of the cathodic i - V profiles originated from ohmic potential drop (see Section 1.5.2.4) in the oxide films on Pt, Rh or Pd was also considered theoretically in this work⁹², but the behaviour predicted for such effects was shown to be inconsistent with the shape of the experimental i - V curves at Pt.

Most of the theoretical calculations for surface processes made in recent years have been carried out by Laviron⁷⁹⁻⁸⁷ who treated cases where no diffusion occurs during the sweep, i.e., the reactive species are adsorbed. This work is of great value, even though some of his published ideas were reported earlier by others^{31,32,89-92}.

He has calculated and derived equations for current-potential curves for both reversible^{79,85} and irreversible^{80,85} 1-electron electrochemical reactions in linear sweep voltammetry for cases where the reactant and product of the electrochemical reaction may both be strongly adsorbed on the surface. This work originated from studies on the influence of adsorption of reactant and/or product of the electrochemical reaction on polarographic currents at Hg. Calculated i-V profiles for reversible or irreversible processes, obtained for conditions of no diffusion of either the reactant or product, were the same as those derived earlier by Conway and Gileadi³¹ and by Srinivasan and Gileadi⁹⁰. The theoretical equations describing these current-potential profiles were derived^{79,80,85} and a useful generalized function was presented^{79,80}. A thorough review of adsorption effects in a simple 1-electron electrochemical reaction in polarography and in linear potential sweep voltammetry, when diffusion of species is, or is not, significant, was also published by Laviron⁸⁵.

Later, Laviron extended his initial theoretical treatment of the simple 1-e reversible reaction by including lateral interaction effects on the surface^{86,87}. He considered that the apparent activation energy changes linearly with changing surface coverage θ , i.e., Temkin adsorption behaviour applies. It seems that Laviron was unaware that this treatment for the simple electrochemical reaction with interactions between the adsorbed species, following the Temkin isotherm, had already been dealt with and the results of such calculations published in almost identical form by Conway and Gileadi³¹ about 12 years earlier. Most of the conclusions reached by Laviron are identical

with those given by Conway, Gileadi and Dzieciuch⁹³ and Conway and Gileadi³¹ earlier. Laviron, using "his" theoretical conclusions for the case when interactions between adsorbed species are significant, was then able to explain some anomalies in experimental polarographic results⁷⁵⁻⁷⁸ on the basis of the interaction effects mentioned above.

1.5.2.2 Theoretical treatments for more complex reaction mechanisms

Use of the linear potential sweep method is not restricted, in electrochemical surface studies, to the case of 1-e surface processes such as have been discussed above. In recent years, various workers have started to consider more complex reaction sequences. For such cases, diagnostic criteria for the kinetic behaviour of surface processes having various mechanisms must be derived and any characteristic behaviour, which differs from that of the 1-e surface process, must be deduced.

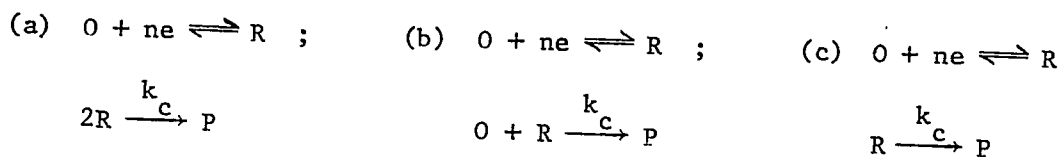
Most of the complex reactions considered have been those where a certain type of chemical reaction either precedes or follows an electrochemical one. Reactants and/or products of one and/or both of these steps are assumed to be adsorbed on the electrode surface, according to a given isotherm governing the behaviour of the adsorbed species.

A theoretical study of the peaks generated by the potentiodynamic sweep technique for the case where a reversible electrochemical reaction is followed by a chemical reaction of a given type was made

by Laviron⁸¹⁻⁸⁵ and by Koutecky and Hanus⁹⁴. The mathematical treatment was given for three cases, as follows:

- (a) dimerization of the intermediate product of the electrochemical reaction^{81,84,85}, adsorbed on the electrode surface;
- (b) coupling, where an adsorbed reactant and the intermediate product of the electrochemical step (also adsorbed on the electrode) react together yielding another product^{82,84,85};
- (c) the adsorbed intermediate produced in the electrochemical reaction step undergoes an ordinary first-order reaction yielding the final product⁸³⁻⁸⁵.

These cases are represented by the following reaction schemes:



In each case, it was assumed that the electrochemical reaction is completely reversible (and both the reactant and the product of this reaction are strongly adsorbed on the electrode surface) as indicated in (a), (b) and (c) above. The adsorption of both species was assumed to be rapid and to obey a Langmuir isotherm. The chemical reaction (following the electrochemical step) was considered to be the rate-determining process (i.e., no backward reaction in this step was considered in each of the cases discussed). The product of the chemical step for all three cases was also assumed to be strongly adsorbed, so that the number of molecules which may diffuse away from

the electrode is negligible in comparison with the number which remain adsorbed at the electrode surface and react. Equations for the current-potential profiles were derived and analytical solutions obtained for all three cases.

It should be mentioned that the elegant analytical solutions that can be derived for some of these cases can only be obtained if the electrochemical step in the sequence is at all times taken (unrealistically) to be reversible, and no back reaction in the chemical step is considered (often an unlikely condition). This, therefore, introduces severe restrictions in the applicability of the treatments presented which can be avoided by more general numerical computations. The kinetic behaviour found for these cases usually depends on the extent to which the chemical steps in (a), (b) and (c) can proceed (with the electrochemical step at quasi-equilibrium) in the time elapsed corresponding to the relative duration of a sweep, measured by the ratio $(s/k_c)^{-1}$, where k_c is the rate constant of the chemical step.

The shape of the i - V profile, the variation of V_p and i_p as a function of the ratio s/k_c were investigated by Laviron. The current-potential profiles for the above reaction mechanisms appear at progressively more negative potentials with increasing s/k_c ratio. This is to be expected, since for smaller s/k_c ratios, the chemical reaction can proceed more significantly during the time of the sweep. The opposite is true for high s/k_c values. Under these conditions, the time elapsed during the sweep is too short for any significant extent of chemical reaction to occur so that the i - V profile for an ordinary 1-electron electrochemical surface reversible reaction is exhibited.

The shape of the i - V profile when s/k_c is small, depends on the reaction mechanism considered. For reaction sequence (a), the profile remains symmetrical, but the half-width decreases from 90.6 mV to about 47 mV for $n=1$ and the value of i_p increases to twice the limiting value it would have when $k_c = 0$, as s/k_c decreases. At the same time, the value of V_p shifts 30 mV (for $n=1$) more anodic per decade of s/k_c which must be small enough for the curves to be past the transitional region, which spans about 6 decades, corresponding to significant or insignificant participation of the chemical step.

For reaction mechanism (b), the current-potential profile does not change shape as s/k_c is changed and remains symmetrical; thus, the value of $\Delta V_{1/2}$ does not vary and is equal to $90.6/n$ mV, the value for the reversible 1-e surface reaction. Only the magnitude of the current maximum varies and it decreases to half the value for the normal peak, i.e., when $k_c = 0$. The transitional region spans three decades only as compared to case (a) and the shift of V_p , for sufficiently small values of the ratio s/k_c , is $60/n$ mV per decade.

Reaction mechanism (c) gives rise to i - V curves which become less and less symmetrical as the s/k_c ratio decreases; also the half-width decreases from $90/n$ mV to $66/n$ mV at the same time. The peak current increases about 1.47 times ($4 e^{-1}$) from the value of i_p , corresponding to $k_c = 0$, over about 4 decades of s/k_c which represents the transitional region. The shift of V_p for low values of s/k_c is 60 mV for $n=1$ per decade of change of s/k_c .

The peak of the back reaction current for the three reaction mechanisms depends on the same parameters as those for the forward peak and on a new parameter, the initial potential of the reverse sweep. For very high s/k_c ratios, an anodic current profile appears and is the mirror image of the cathodic one. As the s/k_c ratio diminishes, the height of the anodic peak decreases until no current is observed, provided that the initial potential of the reverse sweep is negative enough.

Methods for evaluation of the chemical rate constant for the cases considered were described and the appropriate equations were derived. It was pointed out that it is the absolute value of the ratio of the backward peak current to the forward peak current, together with the applied sweep-rate, which allows the value of the chemical rate constant, k_c , to be evaluated.

The most important characteristic features of these reaction mechanisms which allow distinctions to be made between the different cases, can therefore be summarized as follows:

- (i) the effect of the ratio s/k_c on the peak shape and the peak current;
- (ii) the dependence of the peak potential, V_p , on s/k_c ;
- (iii) the shape of the peak for the reverse process and its dependence on s/k_c and the initial potential in the reverse sweep.

The case where a reversible electrochemical reaction is followed by a chemical reaction, the product of which desorbs irreversibly from the surface thus regenerating free surface sites, was

dealt with by Baticle et al.⁹⁵. They assumed that the chemical reaction causes only liberation of free surface sites, previously occupied by the species resulting from the preceding electrochemical reaction, without any other chemical change occurring. The activity of the regenerated sites was considered unchanged. Interactions between the adsorbed species, or heterogeneity of the electrode surface, were assumed to be negligible, so that the conditions corresponded to Langmuir adsorption.

From the theoretical calculations, the simulated current-potential profiles for a range of sweep-rates were obtained and compared with the behaviour of an ordinary electrochemical reaction, i.e., when the rate constant for the chemical step is zero. The effects of changing sweep-rate on the current maximum, i_p , and on the potential for the maximum current, V_p , were evaluated. The theoretical equations for obtaining i_p and V_p were also derived and the limitations of these equations discussed in detail. The effect of sweep-rate on the current-potential profiles for this reaction mechanism, and the conditions under which the current peak is or is not seen, were also mentioned in this work.

Since the above "ec" type of surface reaction can occur during the early stages of oxidation of metals, extensions of this type of treatment were made by introducing additional sequential electrochemical reaction steps⁹⁶ where each, or both, reactions could be followed by a chemical dissolution process⁹⁷. In the former paper⁹⁶, Baticle et al. considered first the behaviour of two successive

1-electron electrochemical reactions, without any chemical reaction present, under triangular voltage sweep conditions. In their calculations, it was assumed that adsorption is fast and there are no interactions between the adsorbed species (Langmuir conditions). In each oxidation process, there is an irreversible step which determines the rate of the overall reaction. It should be mentioned that these authors⁹⁶ considered a mechanism where the transfer of the first electron in each of the overall reactions is the rate-determining step with subsequent electrons (in their mechanisms) being transferred reversibly. Equations, corresponding to the two steps of irreversible transfer, were solved numerically and the overall current-potential profiles, as well as the profiles corresponding to individual electrochemical reactions, were generated.

The case where each oxidation process may or may not be associated with a simultaneous chemical dissolution of the surface oxide formed was also dealt with by Baticle et al⁹⁷. Four reaction models were considered and, in each, a different reaction sequence involving the steps of chemical dissolution of surface oxides, was considered. Equations, for the four cases considered, were solved numerically and characteristic current-potential profiles were demonstrated for each case as a function of sweep-rate.

A case where a chemical reaction precedes the electron transfer reaction has been considered by Alquié-Redon et al⁹⁸. Using the hydrogen (H_2) oxidation reaction as an example, they simulated the capacitance-potential curves for a second-order chemical surface reaction (dissociative chemisorption of H_2 giving $2H$ thus requiring a $(1-\theta_H)^2$ term in the kinetic equation) coupled with a

simple charge-transfer reaction ($H_{ads} \rightarrow H_{aq}^+ + e$), using the appropriate set of differential equations and solving them numerically. Analytical solutions were obtained for two limiting cases: (a) when the electrochemical reaction is in quasi-equilibrium or (b) when it is completely irreversible. Exact expressions for i_p and V_p , as a function of sweep-rate, were derived and it was shown how a first-order chemical reaction can be distinguished from a second-order one.

1.5.2.3 Application of theoretical treatments to oxygen adsorption on noble metal electrodes

The theory of two successive 1-electron transfer steps⁹⁶ in cyclic voltammetry and its application to electrochemical oxygen deposition on the platinum electrode was discussed by Appleby^{99,100}. He reviewed and extended equations describing a single, 1-electron electrochemical reaction under both reversible and irreversible conditions for Langmuir and Temkin isotherms^{90,92} to cases involving multiple step reactions⁹⁹. In particular, two irreversible successive electron-transfer reactions were assumed, viz., $Pt + H_2O \rightarrow PtOH + H^+ + e$ and $PtOH \rightarrow PtO + H^+ + e$ and the conclusions reached were then applied to the problem of formation and reduction of adsorbed oxygen films on Pt in acidic media. Equations for the above two electrochemical charge-transfer steps were derived. Appleby assumed that the Temkin terms in the kinetic equations depend on the total coverage which was shown¹⁰¹ to be unsatisfactory; this is because in most cases only a shift, on the potential scale, of the i - V curve corresponding to the second

electrochemical reaction, results. Also, its shape is always that corresponding to the Langmuir term. The coverage exponent in the rate equation was written⁹⁹ in terms of total coverage and the g factor as follows

$$g(\theta_1 + \theta_2 - 0.5) \quad (1-20)$$

but it is unclear what the significance of the 0.5 term is in his representation.

In order to derive a C-V profile which looks like the classical broad, almost flat-topped pseudocapacitance profile for oxygen adsorption, the value of g in the first reaction forming PtOH, which would have to be used, is near 40. However, this value is much too high even for an adsorbed organic species. It seems that the author did not appreciate this point for he concluded that: "The difficulty with this interpretation is that the calculated peak shape does not exactly reproduce that experimentally observed, e.g.,^{66,102}, which shows a dip following an initial peak." He therefore suggested that the rate constant for the first reaction should be made coverage-dependent, e.g., due to place exchange⁶⁵ where surface rearrangement occurs. The resulting simulated C-V curve shows a peak followed by a dip, but the shape of the anodic curve is still far from that of the experimental curve, which is comprised of more than two peaks. Nevertheless, Appleby concluded that these simulated peaks show many of the features of the experimental curves.

A similar theoretical analysis of the cathodic i-V curves was also given. In order to explain the cathodic reduction behaviour

where hysteresis is exhibited, the second anodic electrochemical reaction corresponding to formation of "Pt-O" from "Pt-OH", was assumed to be in quasi-equilibrium, but with a standard electrode potential for the surface process³⁰ more cathodic than that corresponding to the first oxidation step. This is necessary if the appearance of two cathodic peaks (representing the two single-electron steps, which are not normally observed) is to be avoided.

In a later paper¹⁰⁰, Appleby discussed other models which were proposed to account for the anodic oxidation process on noble metals, especially platinum. He concluded that the model he had proposed⁹⁹ seems to be the best one, since it is consistent with the experimental data obtained. However, the proposed models of Tilak, Conway, Kozłowska and Sharp^{66,102} where three superimposed peaks, respectively corresponding to half-coverages of sub-lattice states "Pt₄OH", Pt₂OH" and "PtOH", seems to be a more realistic one because it can explain the experimental curve for anodic oxidation of Pt much better. This model^{66,102} will now be discussed in more detail.

Theoretical calculations which enabled simulation of current-potential curves for formation and desorption of the oxide layer on platinum to be made were reported by Tilak, Conway and Kozłowska^{102,103}. These calculations gave agreement with the experimental current-potential curves better than the ones derived by Appleby^{99,100}. The observed i-V profile can be quite accurately simulated by computer calculation assuming three sub-lattice stages corresponding to occupancy of the Pt substrate lattice in the ratios Pt₄OH, Pt₂OH and PtOH on the (100)

plane or Pt_3OH , Pt_2OH and PtOH on the (111) plane. Kinetic equations for this model were set up and solved by a standard backward finite-difference integration technique³⁶⁻³⁹.

Even though Tilak et al.¹⁰² were able to simulate the potentiodynamic i-V profiles for the anodic and cathodic processes involved in Pt surface oxidation and reduction, respectively, a complication in their calculations is that different sets of differential equations must be used for simulation of anodic and cathodic profiles on account of the change of state of the oxide film due to place-exchange rearrangements⁶⁵. In fact, the latter process occurs both in the anodic and cathodic reactions and it is this "chemical" reaction which gives rise to hysteresis, and should also be taken into consideration when the equations for the anodic reaction of oxidation of the Pt surface are set up. Further discussion of this problem will be given later in this thesis. It should be pointed out that this rearrangement process can be indirectly observed experimentally and was shown to depend logarithmically on time^{104,105}.

Despite the above mentioned complications, these authors¹⁰² were able to simulate both the anodic and cathodic i-V profiles. The calculated anodic i-V profile, obtained with a proper set of Temkin parameters g and an appropriate set of standard electrode potentials³⁰ for each reaction step in the sequence, matched very closely the actual experimental curve. However, at relatively high potentials the simulated anodic currents fell in comparison with the experimental behaviour because no further degree of oxidation beyond "PtO" was considered.

The explanation of the cathodic i-V profile for reduction of the Pt surface still, however, leaves much to be desired. Remaining questions which need to be answered are:

- (i) the significance of the apparently single* cathodic peak.
- (ii) the movement of this peak to less positive potentials in i-V profiles for reduction of more highly oxidized platinum surfaces.
- (iii) the Tafel slopes for the reduction processes expressed as $dV_p/d \log s$.

It was shown that the observed single cathodic peak can be represented kinetically in terms of a two-stage reduction of the rearranged "OPt" to Pt via an "OHPt" state. From the theoretical calculations, it is apparent that when the surface standard electrode potential, E° , for "OPt" is less positive than the one corresponding to "OHPt", then only a single peak is obtained. (Two peaks are observed when $E^\circ_{\text{OPt}} > E^\circ_{\text{OHPt}}$) cf.⁹⁹. To get a narrow single peak, the process of reduction of "OPt" species to "OHPt" must be in quasi-equilibrium and reduction of "OHPt" to bare Pt surface must be the rate-determining step. A Tafel slope of 40 mV is obtained when the above conditions are assumed and this was observed by Gilroy and Conway¹⁰⁴ experimentally. However, the 40 mV slope was later found to be a special case since slopes between 20 and 40 mV can be observed, depending on the oxidation state of the Pt surface.

* At low temperatures and high sweep-rates, reversible and irreversible components of this peak can be resolved corresponding to the initially deposited OH and place-exchanged OH and O species at Pt.

It seems, from the above, that the kinetic theory of formation and reduction of surface oxides, not only on Pt but other noble metals (e.g., Au, Ru, etc.), as well, discussed by Tilak et al.¹⁰² enables a better understanding of the real reaction mechanisms which are involved in electrode surface oxidation to be gained. However, further improvements to the theoretical calculations and more refined assumptions regarding the reaction mechanisms in question are still needed to provide a better account of the experimental behaviour.

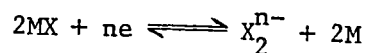
1.5.2.4 Theoretical studies of effects of resistance on the current-potential profiles for a surface process

In potentiodynamic sweep experiments, the possibility of ohmic resistance being developed in an electrochemical cell, when a potential between two electrodes is applied, is a common problem. This effect arises especially at high sweep-rates when currents are large. Even though electronic instruments have been developed to compensate for ohmic resistance, they cannot completely eliminate its effects. Thus any uncompensated cell resistance affects the shape of current-potential curves obtained in an experiment. A matter of special interest here is when such ohmic effects arise because of resistance of a surface film itself.

Recently, de Tacconi et al.¹⁰⁶ and Calandra et al.¹⁰⁷ described mathematical treatments of current-potential profiles obtained by means of the triangular voltage scanning method for a simple first-order electrochemical reaction, when ohmic resistance of the electrochemical cell was included.

De Tacconi et al.¹⁰⁶ presented a complete derivation of current-potential profiles for reaction (I) (see page 34) both for quasi-equilibrium and irreversible conditions when ohmic resistance effects were significant. The current-potential curves for various values of ohmic resistance and the resulting shifts of current maxima and potentials for these maxima were derived for the quasi-equilibrium and irreversible cases. The general features of the current-potential curves for these cases are (a) a decrease of the height of current maximum, i_p ; (b) a shift of potential corresponding to the i_p value to more positive values; (c) an increase in the half-width $\Delta V_{1/2}$ and (d) the shape of i - V profiles becoming more asymmetric with increasing ohmic resistance. When the ohmic resistance is set to zero, the i - V profile obtained earlier by Srinivasan and Gileadi⁹⁰ is, of course, recovered.

In the latter part of their paper, these authors showed that the ohmic drop correction depends also on the order of the electrochemical reaction; they demonstrated this quantitatively by considering a second-order electrochemical process under irreversible conditions, represented by the desorption and electrochemical reduction of an adsorbed species according to the following reaction



The difference between the current-potential profiles for the first-order and second-order processes was clearly demonstrated.

It is to be noted that derivation of kinetic data from i - V profiles obtained by the potential-sweep method will be in error if ohmic resistance effects are significant. Fortunately for studies on oxide films on noble metals, these effects are negligible as the oxide films are usually either good conductors or thin enough for direct electron tunneling to occur.

In a later paper, Calandra et al.¹⁰⁷ extended the treatment of the ohmic resistance effect¹⁰⁶ referred to above to its influence in the potentiodynamic current-potential profiles for a film formation process, where the change of the ohmic resistance is produced by the spread of a reaction product as a layer on the electrode surface as in many anodic dissolution-precipitation processes, e.g., in formation of $PbCl_2$, Hg_2Cl_2 , etc. This film formation process can proceed in two stages: first, the solid layer was assumed to spread to constant thickness across the electrode surface; then an increase of the layer thickness occurs. The rate equation for such an electrochemical process was derived together with equations for the maximum current and the potential at this current maximum. It seems, however, that the derivation for the current-potential profiles in this work is not correct because the rate equation written by the authors did not contain any exponential term in the potential, as is required for the case of an ordinary electrochemical reaction⁹⁰ regardless of whether ohmic resistance¹⁰⁶ is or is not included in the overall measured or controlled potential, or in the kinetic equation. The derived theoretical i - V curves¹⁰⁷ were compared with experimental results for

several systems: (i) formation of insoluble parathiocyanogen on Pt and (ii) precipitation of a solid CuCl layer during Cu dissolution in aqueous HCl solution; quite good agreement was demonstrated despite the fact that the equations used were not of the correct form, as mentioned above.

In an earlier paper by Goldberg and Bard¹⁰⁸, the effect of solution resistance in potentiostatic and galvanostatic experiments was also considered. Simulations of potential-time and current-time profiles were made for cases where non-uniform current densities result from high electrolyte resistance.

1.6 Electrochemical Surface Processes Involving Nucleation and Growth Mechanisms

The possibility that some processes where a surface film is grown involve a nucleation mechanism must be recognized. Since this mechanism must be distinguished from that considered earlier where a monolayer film is grown by random deposition of atoms or radicals, it will be useful to review the features of nucleation processes as they can be involved in surface phase growth.

1.6.1 Nature of nucleation processes

The role of nucleation in electrochemical phase growth processes was recognized early by Volmer and co-workers with regard to metal deposition^{109,110}. Various treatments have since followed and are based on growth of circular-cylindrical and hemispherical elements

of multilayer surface phases such as arise in anodic formation of calomel and metal oxides. Two-dimensional surface nucleation, i.e., formation of edges or steps on a plane surface by aggregation of ad-atoms or ad-ions, is another related kinetic process which must also be considered. Nucleation provides new sites for crystal building by aggregation of the initially deposited adsorbed species. Near the reversible potential, a sufficient number of growth sites may be spontaneously present due to intrinsic defects, that a low growth rate can be sustained. However, nucleation and growth becomes a much more probable process at higher overpotentials, where the surface concentration of deposited ad-atom species (nuclei) can become much increased. The embryonic nuclei, i.e., the nuclei of radii less than the critical radius, may be regarded as forming and breaking up continuously, until they reach the critical size, when a favourable fluctuation will cause them to grow indefinitely. The critical free energy of formation of nuclei, which is characterized by a "nucleation overpotential", thus contributes to the free energy of activation of the deposition process.

The investigation of nucleation-controlled growth of electrodeposits cannot conveniently or practically be made by steady-state techniques. A.C. impedance and potentiostatic pulse methods have therefore been employed in previous experimental work, e.g., ^{111,112}.

The forms of potentiodynamic current-potential (i - V) profiles for surface processes involving random electrochemical adsorption and desorption of species up to monolayer coverage, as in underpotential

deposition, which arise in response to a potential-sweep linear in time, are of general interest (see Section 1.5.2). The question arises as to what will be the potentiodynamic response of a two-dimensional surface process when the kinetics are controlled (a) by growth from nuclei which already exist initially on the surface and/or (b) by growth from, and simultaneous generation of new nuclei. The two-dimensional surface process can be deposition of a species up to a monolayer (and sometimes beyond) or desorption of a species, e.g., in reduction of a surface oxide by an "hole" mechanism. Thus oxide reduction or electrochemical oxidative desorption of metallic monolayers may in some cases proceed by a nucleation mechanism in which holes are formed and then grow across the monolayer.

A number of models for both two- and three-dimensional nucleation and growth processes have been considered. Avrami was one of the first who derived a general mathematical analysis of the geometrical problems arising in the kinetics of phase growth and, in particular, when a series of spheres grow from nuclei and eventually overlap¹¹³. Avrami's mathematical analysis and ideas on nuclei formation and growth in electrocrystallization were recently reexamined by Rangarajan from a probability point of view¹¹⁴. Mathematical derivations for both monolayer and multilayer formation using the probabilistic approach were given. It should be pointed out that multilayer formation was assumed to proceed as a cascade process.

The method of solution for two- and three-dimensional nucleation and growth problems, based on the concept of "additivity of

expectation", was discussed in detail by Evans¹¹⁵. He also considered that the expanding circles or spheres resulting from growth at nuclei, eventually overlap and the growth then continues only at the remaining perimeters of the non-overlapping parts. The concept of "expectation" has proved useful¹¹⁵ in providing a fast mathematical solution of otherwise quite difficult problems. In this treatment, the probability that a certain representative point on the surface remains uncovered is equal to the fraction of the remaining free surface; this probability can also be expressed by Poisson's formula. The "expected" number of, e.g., circles which would pass over the above mentioned representative point in a given time is obtained by averaging the "expected" number after an infinite number of counts¹¹⁵. Treatments of crystal grain-size of metals and development of surface films of corrosion products on metal surfaces were given by Evans¹¹⁵ in the light of his models. Hudson¹¹⁶ applied similar ideas to the treatment of supersaturation phenomena involved in the two-dimensional condensation of adsorbed gases and in particular to the kinetics of such processes.

Recently, Milchev and Stoyanov¹¹⁷ considered "classical" and "atomistic" models for the formation of the critical nuclei in electrolytic nucleation. The "classical" model uses macroscopic quantities such as overpotential, overall work of formation of nuclei, for characterizing the critical nucleus and the number of atoms in it, whereas the "atomistic" model does not employ macroscopic values but rather uses the microscopic properties of the individual atoms which are contained in these critical nuclei. The available experimental

data on electrolytic nucleation on the basis of both of the above models was interpreted both qualitatively and quantitatively. The authors indicated that the quantitative treatment of the experimental data would conform closer to the atomistic model of nucleation, rather than to the classical model. However, it was pointed out that the equations arising from classical theory also appear to be applicable, especially in the cases of nucleation at low degrees of supersaturation.

1.6.2 Review of relevant previous work

It is of interest to review several of the more important papers which have been published in recent years on nucleation mechanisms in electrode processes. As mentioned above, most of the experimental work has been done by potentiostatic pulse techniques.

Fleischmann and Thirsk¹¹¹ discussed in detail the theory of the growth of multilayer deposits on electrodes and how such growth is controlled by at least two different rate constants, which are potential dependent. The two rate parameters correspond to the nucleation rate constant and the rate constant controlling the subsequent crystal growth. Theoretical derivations of equations for one-, two-, and three-dimensional growth have been made for the potentiostatic pulse case. The experimental results obtained for electrodeposition of PbO_2 on a Pt surface and of AgCl on an Ag electrode were compared with the predictions of the theoretical treatments mentioned above and were explained in the light of these derivations. For two-, and three-dimensional cases, growth by expansion of cylindrical and hemispherical elements of the surface phase was assumed, respectively.

In a later paper¹¹⁸ the same authors gave a complete mathematical derivation and equations for both two-dimensional and three-dimensional growth either from a constant number of nuclei or from a number of nuclei which increases with time even though the potential is held constant. Equations for the special case where it is assumed that the crystal can grow only to the height of one monolayer was also considered together with the possibility of overlapping between the growing centres.

Simulation of electrochemical growth of three-dimensional nuclei under diffusion conditions in a potentiostatic pulse was made by Davison and Harrison¹¹⁹. An exact analytical solution for current growth of instantaneously nucleated right-circular cones, including their possible overlap, was given. This model was then extended to the case where diffusion is also included. A method for comparing experiment and theory was also discussed in this paper.

The anodic behaviour of mercury in hydroxide ion solutions was studied by Armstrong et al¹²⁰. The current versus time profiles for formation of HgO on Hg in basic media were shown to depend on the overpotential. At low overpotentials, only a monolayer or mercuric oxide was formed whereas at higher overpotentials, a current peak corresponding to multilayer formation and having an area under the curve which depended on the overpotential applied, was observed. These authors showed that the i-t profiles which corresponded to formation of only a monolayer, i.e., at low overpotentials, arise due to progressive two-dimensional nucleation. For the multilayer peak,

it was assumed that the growth occurred in three-dimensions through development of an array of right-circular cones. The equation for current as a function of time for this type of growth was derived¹²⁰.

The transient and steady-state responses of electrodes under conditions where two-dimensional nucleation in electrocrystallization is rate-determining were considered by Armstrong and Harrison¹²¹. Both potentiostatic and galvanostatic conditions were treated and the appropriate kinetic equations derived. The conclusions from their work were that evidence for two-dimensional nucleation must be sought from transient experiments, especially under potentiostatic conditions, since the steady-state response for metal deposition does not give rise to any characteristic features when the formation of two-dimensional nuclei is rate-determining.

Recently Armstrong and Metcalfe¹²² simulated the current-time behaviour for nucleation on successive two-dimensional layers (cf. Kaischew and Budevski¹²³) under potentiostatic conditions. Numerical integration was used to perform the calculations for nucleation and growth up to the first 50 layers. These authors showed that the current-time transient for layers beyond the tenth would be close to a Gaussian function. The overall i - t profile is seen to give a constant current which is independent of time for these layers.

Two-dimensional nucleation in electrocrystallization, especially of metals, has been thoroughly treated by Kaischew and Budevski¹²³. In their review, the theories of crystal growth on perfect and imperfect planes are discussed in detail. Following a

theoretical discussion, these authors give experimental evidence for a two-dimensional nucleation mechanism for growth of a silver deposit on perfect crystal planes. When screw-dislocations are present on the surfaces, these affect the crystal growth and dissolution so that experimental deviations from perfect two-dimensional nucleation behaviour is observed. Electrolytic phase formation or the heterogeneous nucleation in electrocrystallization of metals was also discussed. An experimental verification of the basic relationship of this theory is also mentioned.

Toshev and Mutaftschiew¹²⁴ studied the open-circuit dissolution of the oxide film which covers a platinum electrode in the presence of nitric acid. The electrolytic nucleation of mercury on a single-crystal platinum surface served as a method for the study of the state and the behaviour of the electrode surface. The activity of the Pt electrode with regard to the nucleation process was found to increase with increasing concentration of the nitric acid and of the time of treatment of the electrode.

Experimental aspects of nucleation-controlled growth were investigated for the case of electrodeposition of Pd on carbon electrodes by Bell and Harrison¹²⁵ who used both the potentiodynamic and potentiostatic techniques. They showed that the formation of nuclei depends on the applied potential, as would be expected. From the potentiostatic transients, these authors deduced that the electrodeposition of Pd gives rise to progressive nucleation and growth in three dimensions.

In a very recent paper, Gilroy¹²⁶ treated the logarithmic time-dependence of growth of very thin layers (1-2 monolayers) of oxide on Pt electrodes in terms of a nucleation mechanism based on equations derived by Fleischmann and Thirsk¹¹⁸. In a number of other respects, the behaviour of the surface oxide at Pt is more consistent with random deposition of OH and O species rather than with a nucleation and growth process so that his treatment requires further examination.

Metal deposition on amalgam surfaces was studied by Harrison and Thompson¹²⁷ and they attempted to establish whether two-dimensional or three-dimensional nucleation and growth occurs on the amalgam when Pb, Au and Cd are deposited. The technique used, again employed potentiostatic pulses. Their conclusion was that all three metals are deposited on Hg by a three-dimensional nucleation and growth mechanism.

Morcos investigated the electrochemical nucleation of Hg on graphite electrodes galvanostatically¹²⁸. This technique, however, does not seem to be very ideal; this is because the overpotential changes nonlinearly with time for various fixed current densities so that the rates of growth and formation of new nuclei vary with overpotential. Hence, determination of the rate constants for the two distinct processes (i.e., the nucleation and the growth steps) becomes exceedingly complicated. For the potentiostatic case, the overpotential is kept constant and in the potentiodynamic sweeps where the overpotential varies linearly with time, it is much easier to determine these rate constants.

Electrochemical nucleation from molten salts was investigated by Hills et al¹²⁹. Using cyclic voltammetry, potential-step and chronopotentiometric methods, these authors were able to study the electrodeposition of silver on Pt electrodes from solutions in the molten nitrate eutectic $\text{NaNO}_3\text{-KNO}_3$ and showed that deposition of the metal is controlled by nucleation processes. To investigate the kinetics of the nucleation step, the double-pulse potential-step method was used. Similar results were obtained for systems such as silver on platinum or graphite when the electrodeposition occurred from aqueous solutions.

The frequency-dependence of electrode impedance for two-dimensional nucleation and growth was considered by Armstrong and Metcalfe¹³⁰. Current-time profiles for the potentiostatic case which arise after applying a small perturbation in the form of a change in either or both the nucleation rate and the rate of growth of the circles, were simulated for development of a monolayer. The behaviour of the multilayer case was obtained simply by a recurrence relationship. To obtain the impedance frequency response, a Fourier transform of the potentiostatic transient signal was utilized.

Some other relevant papers which have appeared in recent years¹³¹⁻¹³⁵ have treated nucleation and growth both from the experimental and theoretical points of view. The experimental results obtained for the various systems studied were treated on the basis of various theoretical models previously proposed which have been reviewed earlier.

CHAPTER II

SUMMARY OF THE AIMS OF THE PRESENT WORK

In the foregoing review of previous theoretical work on electrochemical surface processes, including that done earlier in this laboratory^{31,32,89}, it has been shown that the most extensively treated case is that for the 1-e surface process involving a single adsorbed species. For certain conditions, the way the behaviour of such a process is modified when coupled with a chemical step in various ways has also been treated, but mainly from the polarographic point of view⁷⁹⁻⁸⁷ and with severe restrictions regarding reversibility of the steps.

In the new work to be described in this thesis, it has been the aim to provide numerical computations leading to simulation of the electrochemical kinetic behaviour of various reaction mechanisms and/or conditions, e.g., of reversibility or irreversibility of the steps, for which analytical solutions to the kinetic problems cannot be obtained. It has been considered desirable to present the conclusions of these calculations in terms of characteristic behaviour which can be deduced for various reaction schemes and the consequent kinetic criteria which can be used for their identification when the appropriate experimental behaviour is examined. This is an important aspect of the way the conclusions from the calculations will be presented.

Important conditions which will be examined are: (a) the transition from reversible to irreversible behaviour and (b) the effect of lateral interaction in the layer of adsorbed species characterized by an appropriate parameter of the electrochemical adsorption isotherm.

Applications will be made to several cases of experimental interest, e.g., (a) the difference of behaviour of metal atom deposition in a monolayer (underpotential deposition) and in electrocrystallization involving nucleation and growth (overpotential deposition); (b) the behaviour of surface oxide films on noble metals where deposition of an adsorbed layer of OH or O species is followed by a chemical rearrangement step so that reduction from the rearranged state of the surface oxide film is thus not the reverse of the electrodeposition step; (c) the behaviour of surface reactions when chemical steps are coupled with the charge transfer step and occur before or after it in the overall reaction sequence.

In Chapters IV to X new theoretical work will be presented on the following types of reactions:

- (i) 1-e surface process with a single adsorbed species (treated as a "reference" case);
- (ii) Two parallel 1-e surface reactions;
- (iii) Coupled chemical and electrochemical steps;
- (iv) Dissociative chemisorption step coupled with parallel electrochemical reactions;
- (v) Surface oxidation reactions;

- (vi) Inhibition of a Faradaic reaction by an adsorbed species (e.g., surface oxide) electrodeposited in a parallel reaction;
- (vii) Nucleation-controlled processes.

In Chapter III, which follows, an account of the computational procedures involved in the numerical simulation for the above cases will be given.

CHAPTER III

CALCULATIONS

3.1 Computer Simulation Applied to Studies of Various Electrochemical Reaction Sequences

It has been stressed in Chapter I that electrode surface processes can only be studied in the non-steady state, or by perturbation of equilibrium adsorption conditions, e.g., for evaluation of H or metal atom adsorption. The value of the potentiodynamic method where the potential is varied linearly with time has been emphasized.

The rates of charge transfer reactions that involve deposition or ionization of adsorbed species at electrodes, or of more complex surface reactions, depend directly on coverage of the adsorbed species and on the applied potential. The kinetics of such processes can be expressed mathematically by a set of differential equations corresponding to the appropriate reaction mechanism. These equations are then integrated to give the required solutions (i-V profiles). However, most of the problems can be solved only numerically using computer simulation procedures^{103,136-139}. Only for the case of the simple 1-electron electrochemical reaction under both reversible and irreversible conditions, and assuming that the Langmuir isotherm is followed, can analytical solutions be obtained⁹⁰.

All the simulations were carried out on an IBM 360, Model 65 computer, using a "System/360, Continuous System Modeling Program"-

(S/360 CSMP) developed by IBM^{136,137}. This is a problem-oriented programme, designed to facilitate digital simulation of continuous processes. It provides an application-oriented language that allows these problems to be formulated directly from either an analogue block diagram representation or a set of ordinary differential equations. A basic set of functional blocks, with which different components of a continuous system may be represented, is included in the S/360 CSMP programme^{136,137}, as will be discussed in a later section. Most FORTRAN statements^{140,141} allowing non-linear and time-variant problems of considerable complexity to be handled readily are accepted by this programme. FORTRAN subroutines^{140,141} may also be included. Input and output data are handled using application-oriented control statements¹³⁶ (see Sections 3.3.1.2 and 3.3.1.4). The main advantages of this programme^{136,137} are statement sequencing and a choice of integration techniques¹⁴¹ of which there are six^{136,137} and, if none of the integration methods satisfies the user, he can supply his own integration procedure. In sorted sections, structure statements may be written without any order, since S/360 CSMP will sort them automatically to obtain a proper representation of the physical system to which the problem is addressed.

About 95% of this application program is written in FORTRAN using the FORTRAN IV (Level G) as the source language^{140,141}. S/360 Assembler Language is used for the rest of the package, whose operations are not readily performed in FORTRAN. The whole package is set up in such a way that the user's programmes as well as the calculations must

employ single-precision, floating-point arithmetic, even though the programmes of the application package use double-precision arithmetic, where needed.

3.2 Runge-Kutta Integration Method (RKS)

Various methods are available for iterative integration of first-order ordinary differential equations^{136,138,141} such as are generated in non-steady state electrode-kinetic problems. A method of starting the solution or solving the equation completely is to re-express the integration function in a form equivalent to a Taylor series so that the solution is obtained with an accuracy corresponding to a certain number of terms in the series. Also, it is very useful to obtain the terms in such a series by using a weighted sum formula of the kind employed in a numerical integration. The fourth-order Runge-Kutta method^{136,138,139,141} fulfils these requirements and also has the useful advantage that the integration interval Δt can be readily changed. The Runge-Kutta procedures are single-step ones, i.e., they do not require any past history of values, unlike other methods, e.g., the Milne fifth-order predictor-corrector, Simpson's rule, the trapezoidal rule, etc.^{136,138,141} which are based on the integration of equal-interval interpolation formulae.

The Runge-Kutta technique was applied to the numerical solution of equations such as

$$i = Q \frac{d\theta_B}{dt} \quad (3-1)$$

where θ_B is the coverage by species B deposited in a 1-e surface process (see Chapter IV), $M + A \rightarrow MB + e$, Q is charge for deposition of a monolayer of B and

$$\frac{d\theta_B}{dt} = f(t, \theta_B) \quad (3-2)$$

The method enabled values of θ_B to be evaluated at different times t as well as different potentials, V , since $V = V_{in} \pm st$.

The fourth-order method gives a new $\theta_{B,j+1}$ value in relation to $\theta_{B,j}$ at the present time t_j in the integration according to

$$\theta_{B,j+1} = \theta_{B,j} + \frac{\Delta t}{6} (\lambda_0 + 2\lambda_1 + 2\lambda_2 + \lambda_3) \quad (3-3)$$

where

$$\lambda_0 = f(t_j, \theta_{B,j}) \quad (3-4)$$

$$\lambda_1 = f\left(t_j + \frac{\Delta t}{2}, \theta_{B,j} + \frac{\Delta t \lambda_0}{2}\right) \quad (3-5)$$

$$\lambda_2 = f\left(t_j + \frac{\Delta t}{2}, \theta_{B,j} + \frac{\Delta t \lambda_1}{2}\right) \quad (3-6)$$

$$\lambda_3 = f(t_j + \Delta t, \theta_{B,j} + \Delta t \lambda_2) \quad (3-7)$$

and j represents a stage in the iterative solution. Knowing initial values of θ_B and time t , it is therefore possible to calculate the next value of θ_B at a given new time value $t_{j+1} (= t_j + \Delta t)$ using eqn. (3-3).

The Runge-Kutta procedure is normally stable and self-starting, since only the functional values at a single previous point are required to obtain a value of θ_B ahead. Furthermore, it is easy

to change the step size Δt at any step in the calculations, which is of great importance since it is desirable to minimize errors. On the other hand, each step requires evaluation of the right-hand side of the system four times [eqn. (3-2)], which is a great disadvantage compared with other methods having the same accuracy, since it is time-consuming, particularly if the expression for the first derivative is complicated. A substantial disadvantage of the method is that neither the truncation errors nor estimates of them are obtained directly in the calculation procedure. Therefore, control of accuracy and adjustment of the step size Δt is made by comparison of results obtained by both the Runge-Kutta and Simpson's rule integration methods¹³⁶. The defined interval, Δt , is automatically reduced to satisfy the following condition.

$$\frac{|\theta_{t+\Delta t} - \theta^S|}{AE + RE |\theta_{t+\Delta t}|} \leq 1 \quad (3-8)$$

where θ^S is $\theta_{t+\Delta t}$ calculated by Simpson's rule, and AE and RE are the absolute and relative errors, respectively, which are assigned in the calculation procedure (see Section 4 - execution control statements) and correspond to the particular integrator value.

The theory, given here only for a single first-order differential equation, can readily be extended to a system of such equations. The extension, from one equation to a system, can be achieved by treating θ_B as a vector in the calculation, rather than a single integrator variable. For the reaction mechanisms considered in this thesis, the RKS method was found to be efficient and did not

give rise to any kind of oscillation in θ 's (see subroutine INITTH), but in some cases, however, especially for the more complex reaction mechanisms, a very small oscillation in current, i , still occurred (see subroutine PEAKS). It should be mentioned that this oscillation was observed, if it happened at all, only for reversible reaction conditions. For irreversible cases, no oscillation in the solutions for i occurred.

3.3 Description of the Developed Programme Used in the Simulations

A general programme for solving up to 5 electrochemical and/or chemical reactions both in parallel and/or in series using appropriate sets of differential equations was developed. A representative overall programme for a simple 1-electron electrochemical reaction is shown in Appendix I. The main features of the whole programme will be described using this representative case. It should be mentioned that flowcharts used for developing this programme are not included in the thesis as it is inconvenient to have this volume of material published in the thesis.

The overall programme consists of the main programme, written in S/360 CSMP language, and 8 subroutines written in FORTRAN. It is the CSMP programme which constitutes the major part of the overall programme as it embodies the important tasks of calculations, i.e., primarily solving a particular set of differential equations which represents a given reaction mechanism. The tasks of the subroutines are only secondary ones, as will be discussed and explained in the appropriate sections.

3.3.1 CSMP programme

The CSMP programme (see Appendix I) can be divided into 7 sections. The first four sections contain data statements, translation control, execution control and output control statements¹³⁶. The last three sections represent initial, dynamic and terminal segments of the modelling technique for solving the problems in question.

3.3.1.1 Section 1

In the first section, the size of the variables is defined by determining the appropriate length of the vectors of all the parameters needed in the calculations using the DIMENSION statements. Since the majority of the vectors have dimension 5 this means that only up to 5 differential equations may be solved simultaneously. Also included in this section are the list of all the integer parameters used mainly as counters or flags, and all the numerical values of constants which remain unaltered and are not changing variables from one run to another. The former are listed under the translation control statement FIXED, because otherwise all the variable names assume real (floating-point) values¹³⁶. The latter are contained in the data statement CONST together with the numerical values. These variables include constants like the Faraday constant, "FC", the value of β , "BETA", and the values of universal gas constant, "R", temperature, "TP" (in °K), and the charge for monolayer deposition, "CPCM".

3.3.1.2 Section 2

The second section includes all the variable parameters, i.e., those which could be changed from one run to another one and from one reaction sequence to another. Dimensioned variables are included in the TABLE data statement. This permits data stored in such a one-dimensional array to be identified in structure statements by the location of the data in that array. This statement must appear together with STORAGE, the translation control statement, which determines which variable will appear as a one-dimensional array and how long the array is (see Section 3.3.1.1). Data contained in the TABLE include forward rate constants, "FRC", backward rate constants, "BRC", standard reversible electrode potentials, E° , for the surface processes, designated "ER", the number of electrons transferred in each step of the reaction sequence, "EN", the interaction parameters, g, designated "G", and the sign of the differential equations, "SIGN", (+1 or -1) depending on whether the equations refer to the rate of increase of product or decrease of reactant, with time.

The INCON data statement includes the parameters characterizing the initial conditions which govern a particular reaction mechanism. The parameters are: (a) "IDIR", which indicates whether sweep is going first in the anodic direction (+1) or cathodic direction (-1); (b) "NDIM", which represents the number of differential equations to be solved; (c) "NPRL" tells how many parallel reactions occur first, before any other reaction does and (d) "THI n" give the initial coverages of all the adsorbable intermediate species "n" at time $t = 0$.

The PARAM data statement contains all the values pertaining to a given run. Sweep-rate values are designated "SR" and the initial potential from which the sweep is started is symbolized by "VIN". Both anodic and cathodic potential limits in the sweep experiment are named "VAEND" and "VCEND", respectively. The value of the flag "ICOUNT" determines whether the sweep is done only in the forward (ICOUNT = 1) or both the forward and backward (ICOUNT = 2) directions. The latter applies if the multiplication constant, "CMULT", which multiplies the sweep-rate "SR" to give a new value, is negative. This then means that the sweep is done in both forward and backward directions and the turning occurs at a potential "VCUT". If, however, the value of "CMULT" is positive, but not 1, then it indicates that the sweep-rate is changed during the forward sweep at "VCUT", and no backward sweep is performed. Another important counter is the parameter "IHOLD", which determines whether holding at a given potential is (+1 or -1) or is not (0) done. If the holding is performed, distinction must be made between holding in the anodic (+1) and cathodic (-1) direction. The holding potential is designated "VHOLD" and the length of holding is signified by "THOLD".

3.3.1.3 Section 3

The third section is the MACRO function called "SOLVE". This type of function of S/360 CSMP is a very powerful feature of this language. Using the basic functions which are available in the S/360 CSMP package, it is possible to build much larger functional blocks. It should be mentioned that a MACRO function may be used any number

of times during the simulation calculations, and hence this function operates as a subroutine in ordinary FORTRAN language^{140,141}.

It is in this section that the appropriate set of differential equations, corresponding to a given reaction mechanism, is defined and integrations are performed (see Appendix I, Section 3, for 1-electron electrochemical reaction). The variables, which are of interest in the present work, as well as for further calculations, are defined in the output part of the MACRO translational control statement card. These variables appear to the left of the equals sign on that particular statement card. "THET 1" to "THET 5" are the coverages and "DER 1" to "DER 5" represent the derivatives, or the rates, which are defined as the differences between forward and backward rates of the individual reaction steps in a given reaction mechanism, multiplied by either the Faraday constant or the charge for monolayer formation depending, respectively, on whether a continuous Faradaic or pseudo-faradaic process is considered. The terms "DF n" and "DB n" correspond to the forward and backward rates of the n'th reaction, respectively. The overall rate corresponding to the n'th species is represented by "DTH n", which upon integration gives the value of the n'th adsorbed species "THET n".

3.3.1.4 Section 4

All the execution and output control statements are embodied in Section 4. The execution control statements are used to specify certain items relating to the actual simulation run, e.g., integration

method, integration interval, allowable errors for integrator outputs, etc. Items such as printing and/or print-plotting or cross-plotting the variables, which are of interest in the data output, as well as printing a title at the top of each page of printed output, are embodied in the output control statements.

The execution control statements are: (1) METHOD, (2) TIMER, (3) FINISH, (4) RELERR, (5) ABSERR. The output control statements are: (1) RANGE, (2) PRINT and (3) TITLE.

(i) Execution control statements

(1) METHOD - this label specifies a particular integration technique to be employed in the simulation. S/360 CSMP has seven different integration methods embodied in the package. It is possible to use a user-supplied integration subroutine as well, if it is desired. All the calculations for all the reaction mechanisms studied involved the RKS integration technique which is the standard, fourth-order Runge-Kutta method with variable integration interval^{136-139,141}. In order to assess the error which results in the integration, a Simpson's rule integration technique is used for comparison^{136-138,141}. The Runge-Kutta procedure was discussed in more detail in Part 3.2 (see page 71).

(2) TIMER - this card specifies the values of system variables. It should be mentioned that the specifications

of the system variables are automatically adjusted by the programme, if necessary, to ensure a consistent relationship between run time, output intervals and integration interval. The system variables that can appear on the TIMER card are:

- (a) "FINTIM" - which defines the maximum value of the independent variable and which must be specified for each and every simulation.
 - (b) "DELT" - defining the step size of the independent variable. It is possible for the programme to adjust this parameter in order to satisfy the integration error when using the RKS method.
 - (c) "DELMIN" - which specifies the minimum integration interval that is allowed for the RKS method, which is, as mentioned above, a variable-step integration technique.
 - (d) "PRDEL" - showing the step size required for the output printing.
 - (e) "OUTDEL" - which essentially performs the same task as "PRDEL", but is used when cross-plotting or print-plotting is required.
- (3) FINISH - this feature allows the user to define additional terminating conditions for integration besides the "FINTIM" specification. Using this card it is therefore possible to stop a run when any dependent variable reaches

or crosses some specified limit even before the value of "FINTIM" is reached. It is also possible to terminate a run when two dependent variables are equal or the difference between them changes sign.

(4) RELERR - this card allows a relative error for each integrator output to be defined. It can be used only with integration routines (RKS and MILNE), where the integration interval is allowed to vary in order to satisfy the error limits^{136,141}.

(5) ABSERR - this control statement is very similar to the previous one but controls the absolute rather than the relative errors. It was shown in eqn. (3-8) that the maximum allowable error for each integrator is given as the sum of the permissible relative and absolute errors. It must be mentioned that absolute error dominates when the integrator value approaches zero and relative error takes over as the integrator output value grows in magnitude. Further details of this point were discussed in Part 3.2.

(ii) Output control statements

(1) RANGE - this label is used to obtain the minimum and maximum values of the specified variables reached during a simulation run, together with the values of the independent variable corresponding to these minima and maxima.

(2) PRINT - this card specifies all the dependent variables whose values are to be printed at each "PRDEL" interval, together with the independent variable (time), during the simulation. All the variable names are printed in print-out headings. Since PRINT control card is used with real numbers only, it is necessary to equate any integer variables the printing of which might be of interest, to real variables first, and only then to request the printing of such variables.

(3) TITLE - the statement appearing on the TITLE card will appear as a heading at the top of each page of printed output.

3.3.1.5 Sections 5-7

The Sections 5 to 7 represent the entire simulation programme and each section corresponds to a different segment, i.e., INITIAL, DYNAMIC and TERMINAL. These three segments describe the computations to be performed before, during and after each simulation run, respectively, and they represent the highest level of the structural hierarchy. In the individual segments the user has an option to have the structure statements sorted automatically.

3.3.1.6 Section 5 - INITIAL segment

Frequently a simulation involves initial conditions or parameters which can be expressed in terms of more basic parameters and

the computation needs to be performed only once before the simulation run, rather than repeatedly during the run. It is the function of the INITIAL segment to be used exclusively for computations of these initial condition values.

It is in this section that terms such as b ($b = \frac{RT}{\beta F}$) (see also Chapter I, p.36), initial coverages for reversible reactions (see Section 3.3.2 for detailed explanation) and different switches and flags are set before the actual simulation is performed. It is in this section that "PRDEL", "OUTDEL" and "DELT" are properly defined. They are defined in such a way that the printed increments of changing potential rather than time are constant, because it is the potential which is the important variable in the simulations, and of course in the electrochemistry, as will be seen in later chapters.

3.3.1.7 Section 6 - DYNAMIC segment

DYNAMIC segment represents the nucleus of the continuous simulation system for solving the differential equations that constitute the dynamics of a given model. This segment is the most extensive one, as it contains all the differential equations, which are defined in the MACRO function "SOLVE" (see Section 3.3.1.3), together with all other calculations required during the run. It is in this section in which values of individual currents, total current, total pseudocapacitance, coverages and total coverage of the surface as a function of potential are calculated. In the latter part of this segment, values of total pseudocapacitance and corresponding potential

are stored in order to obtain computer graphical output of pseudo-capacitance-potential (C-V) profiles. This graphical output is used only for a preliminary look at the results. Also, call to a subroutine which determines both maxima and minima of C-V profiles is performed. Finally, another subroutine, which acts like a function generator, is called and tests on the termination are done, together with other mathematical tasks embodied in this subroutine, as will be explained in more detail in Section 3.3.3.

3.3.1.8 Section 7 - TERMINAL segment

The TERMINAL control card allows calculations which are to be done only at the completion of the run, to be performed in this section. Calls are made to four different subroutines, which perform the tasks of printing all the parameters used for a given run, plotting the graphs of C-V profiles and reassignment of the initial parameters which may have been changed earlier in the calculations.

The individual supplied subroutines will be discussed in more detail in the following Sections.

3.3.2 Subroutine INITH

This subroutine is called from the INITIAL segment of the CSMP programme. The purpose of this subroutine is to redefine the initial conditions for coverages, originally set in Section 2 for reversible electrochemical reactions as well as the initial coverages in the chemical reactions which are assumed to be at equilibrium.

The main reason for redefining the initial values of coverages is that some difficulties may arise for reversible electrochemical processes. In the case of reaction (I) (see Chapter IV), for example, the value of θ_B decreases as the initial potential V_{in} is taken more and more negative. Initially, θ_B values were taken as zero, or very near zero, but subsequent integration gave unstable solutions with current, i , and θ_B values oscillating for potentials $V > V_{in}$ during the simulation of the anodic potentiodynamic sweep. Also, in some cases, divergence of θ_B resulted, since the computation accuracy demanded in θ_B was 10^{-6} . This led to the conclusion that θ_B must be known exactly for a given V_{in} value. Knowing that for a reversible electrochemical reaction the derivative $\frac{d\theta_B}{dt}$ must be zero in order to preserve the equilibrium condition, it was possible to determine the exact value of $\theta_{B,in}$ for a given V_{in} value using the equilibrium equation. More generally, the equilibrium method may be applied to the situation where the interaction parameter in the adsorption isotherm is not zero (eqn. (1-5), Chapter I). However, for a given V_{in} value, an iterative procedure having a general form $\theta_{j+1} = f(\theta_j)$ must then be applied where j represents the j 'th iteration being performed. When the difference between the left and right-hand-side was less than a preset error, the value of $\theta_{B,in}$ was assumed to be correct.

For irreversible electrochemical and/or chemical reactions, high precision in initial θ_B values is not any longer required and it is sufficient for the case of reaction (I) to assume the initial coverage $\theta_{B,in}$ to be zero for a sufficiently negative value of V_{in} .

No oscillations or divergence in current values, i , or coverages θ_B at different potentials V greater than V_{in} then arise.

The latter part of the subroutine, "ENTRY RENEW", which is called from the TERMINAL segment, resets the counters and the initial coverages to their original values appearing on the data statement cards.

3.3.3 Subroutine FCNGEN

Subroutine FCNGEN is called from the DYNAMIC segment of S/360 CSMP programme and it embodies the general properties of a function generator. The subroutine consists of three parts. The first part performs the potential-holding operation for a given time specified by parameter "THOLD" at a given potential "VHOLD". It should be mentioned that the printing increment is changed during holding to 1/10 of "THOLD" so that only 10 intermediate times are recorded during holding. The second part tests whether the original sweep is in an anodic-going or cathodic-going direction and performs the reversal of sweep; it also changes the sweep-rate while still going in the original direction or in the reverse direction, at a given potential "VCUT". The values of "PRDEL" and "OUTDEL" are adjusted in such a way that the potential increment (taken as 1 mV) remains always the same. The third part determines if the potential during the sweep is within the limits of imposed anodic and/or cathodic potential settings and, if the changing potential reaches either of the limits, the calculation is terminated (this corresponds to the "IEND" flag being changed from 0 to 1).

3.3.4 Subroutine PEAKS

In more complex reactions, more than one adsorbed intermediate can arise. Then corresponding component currents can be generated. For such cases, both anodic and cathodic overall peak currents, together with the values of individual currents at these peaks, potentials at which the overall peak currents occur, and total and individual coverages of the adsorbed intermediates up to the overall peak currents are determined by means of the subroutine PEAKS. This subroutine may also be used, of course, for a simple surface process involving only one adsorbed species. The programme is quite a simple one. The determination is done by comparing a previous value of current with a present one. If the previous current value is greater than the present one for an anodic-going sweep, a peak is recorded. Similarly, if the previous current value is smaller than the present one for a cathodic-going sweep, a cathodic current peak is registered (cathodic currents are taken negative). For more complex reactions, individual component current maxima and the potentials at which they occur, together with the coverages up these potentials for the individual species, are also recorded in the same manner as described above. As this subroutine is not a perfect one, it does not guard against possible small oscillations, especially for more complex reaction mechanisms under reversible conditions. As the peaks are determined by comparison between two adjacent current values as mentioned above, false "peak" is then recorded. It is then necessary to check the complete output for such a run to find the true peak

maxima. This is not very difficult because most of the oscillations occur at the beginning or the end of the current-potential curves, i.e., at the feet of the curves. However, for simpler reaction mechanisms, this subroutine is adequate and provides the user with correct results; no problems are encountered if oscillations do not arise.

3.3.5 Subroutine PRINT

Subroutine PRINT is used when it is desired to obtain tabular print output at other times than those specified by the system variable "PRDEL". This subroutine is called from the DYNAMIC segment of CSMP programme, subject to logical tests. It is used only when the reversal and/or change of sweep-rate are performed (see Section 3.3.3), because in the vicinity of the above mentioned changes, the values of current might rise or decrease too drastically for them to be observed in the regular print output times. Hence, using this subroutine, better trajectory profiles of i-V or C-V curves are obtained in the regions where sweep-rates are changed.

3.3.6 Subroutine OUTPUT

This subroutine, which is called from the TERMINAL segment of the CSMP programme, causes all the necessary parameters pertaining to a given run to be printed in tabular form. Values such as forward and backward rate constants, standard electrode potentials for surface processes, g-parameters, anodic and cathodic potential limits, initial

potential and sweep-rate used in the run, defined in the data statements section, are printed out. The results for the total current peak maxima, as well as the individual current peaks, together with the appropriate values of potentials and coverages determined in the subroutine PEAKS, are also recorded. If a change of sweep-rate or holding is performed during the run, additional parameters "CMULT", "VCUT", "IHOLD", "VHOLD" and "THOLD" and their numerical values will also be printed.

3.3.7 Subroutine PLTDET

The purpose of subroutine PLTDET, which is also called from the TERMINAL segment of the CSMP programme, is to determine the standard maximum and minimum limiting values of x and y axes. This is done only for graphical purposes. In this way, all the printed graphs of the C-V profiles from different runs are normalized and can be directly compared. Different graphs thus have the same x and y scales or have simple multiples of a given set of x and y ranges, which are defined in this programme. The calculated minimum and maximum values of x and y from the data which are to be plotted are determined and then fed into the next subroutine, which does the plotting on these optimized x,y scales.

3.3.8 Subroutine GRAPH

Subroutine GRAPH causes graphs of pseudocapacitance versus potential (C-V) to be printed for each run performed. The curves are represented by stars (*), each of which represents a point on a given

C-V profile. Minima and maxima for both x and y axes are taken from subroutine PLTDET and utilized to calculate and print the scale indicators. It should be pointed out that the graphs printed by this subroutine were used just to see the rough shapes of the profiles and for comparison with the curves obtained under different conditions (e.g., different sweep-rates, rate constants, E° values, etc.). For publication purposes, the graphs were plotted precisely on graph paper using digital output values obtained in the given run.

3.3.9 Subroutine UPDATE

The structure statements defined in Sections 5-7 of the S/360 CSMP programme, which constitute the whole simulation procedure, must be converted into a FORTRAN subroutine. This translation is done automatically, internally and a generated FORTRAN subroutine UPDATE results. It is only then that this subroutine is compiled and executed together with all the other subroutines mentioned above, as well as with the selected integration routine (RKS) to accomplish the simulation. As the INITIAL, DYNAMIC and TERMINAL segments were discussed already, it is not necessary to try to explain this subroutine because it is just the translation of these three segments defined in the S/360 CSMP portion of the programme.

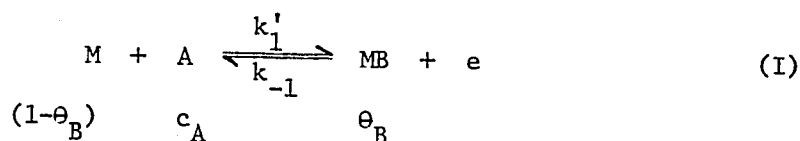
CHAPTER IV

MODEL 1-ELECTRON ELECTROCHEMICAL SURFACE REACTION

WITH A SINGLE ADSORBED SPECIES

4.1 Introduction

In the present chapter, the model 1-e, first-order surface process^{31,90} where free metal surface sites M available at a relative surface concentration $(1-\theta_B)$ react with molecule A from solution to form a chemisorbed species MB on the surface (coverage θ_B), viz. (cf. Chapter I, p.34)



will be examined as a reference case, especially with regard to effects of lateral interactions^{31,93} within the adsorbed layer of B on M on the kinetic behaviour of reaction (I). It is assumed that no diffusion limitations arise in (I). Examples of reaction (I), or its cathodic equivalent, are the deposition of H from H_3O^+ or H_2O , of metal atoms such as Pb, Cu from their ions and of OH or O species from water. Usually reaction (I) involves displacement of a proton since the chemisorbed species B are normally not charged.

The response of this 1-e electrochemical surface process to a linear potential sweep is considered for the cases where the adsorption

of the electroactive species both does and does not involve an appreciable (linear) variation of energy of adsorption with coverage, characterized by the coefficient g [see Chapter I, p.19, eqns. (1-4) and (1-5)], arising from interaction and/or heterogeneity effects.

Procedures are derived for evaluating the characteristic parameters, especially the g factor controlling the adsorption isotherm, for electrochemical surface processes involving electrodeposition of an ad-species up to a monolayer or stripping of monolayers or partially covered surfaces. Most of the cases considered refer to an irreversible surface process but the transition from reversibility to irreversibility, first investigated by Srinivasan and Gileadi⁹⁰, is evaluated for some cases with respect to the value of g involved in the adsorption behaviour of the ad-species. In the reversible case, the relationship of the current-potential profiles to the adsorption pseudocapacitance, previously evaluated^{31,32}, is considered.

4.2 Calculation Procedure and Values of Parameters

All the simulations were carried out on IBM 360, Model 65, using an IBM application programme "System/360 Continuous System Modeling Program" - (S/360 CSMP). Details of this programming language and the integration procedure, together with all the supplied sub-routines, were discussed in Chapter III (see also Appendix I for the actual programme).

All the calculations in this chapter, as well as in others, were made for Q , the charge for generating monolayer coverage of B in

reaction (I), taken as $220 \mu\text{C cm}^{-2}$, as for H on Pt. The symmetry factor, β , for charge transfer was taken as 0.5 as supported experimentally⁵⁶ for reaction (I) when B is H. For convenience, c_A is taken as 1 mol l^{-1} . It should be pointed out that the solution concentration of any soluble species considered in this and other chapters will always be taken as a standard value of 1 mol l^{-1} , unless otherwise stated.

The values of the other constants used throughout all the calculations and for all the reaction mechanisms described in this thesis are:

F - Faraday constant (96490 Coulombs/mol)

R - gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

T - temperature (298.15 K).

4.3 Formulation of Kinetic Equations

For reaction (I), the basic equation for the current density, i , as a function of potential V in the sweep at a rate $s = \frac{dV}{dt}$ is

$$i = Q \frac{d\theta_B}{dt} = Q[k'_1 c_A (1-\theta_B) \exp(\frac{\Delta V}{b} - (1-\beta)g\theta_B) - k_{-1} \theta_B \exp(-\frac{\Delta V}{b} + \beta g\theta_B)] \quad (4-1)$$

where k'_1 and k_{-1} are the rate constants and k'_1 is taken as equal to k_{-1} , thus defining a standard equilibrium condition for which the coverage is 0.5 at the standard electrode potential, E° , with $c_A = 1 \text{ mol l}^{-1}$ (see below). The modulating potential, ΔV , is given by

$$\Delta V = V - E^\circ = V_{in} \pm st - E^\circ \quad (4-2)$$

and $b = \frac{RT}{\beta F} = \frac{RT}{(1-\beta)F} = \frac{2RT}{F}$, ($\beta = 0.5$); E° is the standard electrode potential for the surface process³⁰, which has been taken in all calculations arbitrarily as zero^{*}, unless otherwise stated. V_{in} is the initial potential in the sweep and g an interaction parameter (cf. ref. 93) in the electrochemical adsorption isotherm for B:

$$\frac{\theta_B}{1-\theta_B} = K_I c_A \exp\left(\frac{\Delta VF}{RT}\right) \exp(-g\theta_B) \quad (4-3)$$

which follows from eqn. (4-1) when $i=0$, writing the equilibrium constant $K_I = \frac{k'_1}{k_{-1}} = 1$. As mentioned previously (see Chapter I, p.19) positive values of g correspond to repulsion in the chemisorbed layer and negative ones to attraction.

From eqn. (4-3), after suitable rearrangement, $\frac{d\theta_B}{dt}$ can be evaluated as

$$\frac{d\theta_B}{dt} = \frac{K_I c_A \exp\left(-\frac{\Delta VF}{RT} + g\theta_B\right) \frac{Fs}{RT}}{\left[\exp\left(-\frac{\Delta VF}{RT} + g\theta_B\right) + K_I c_A\right]^2 + K_I c_A g \exp\left(-\frac{\Delta VF}{RT} + g\theta_B\right)} \quad (4-4)$$

noting that ΔV as $f(t)$ is given by eqn. (4-2).

By conventional operations the peak potential V_p at the current maximum, i_p , is readily obtained as:

$$V_p = -\frac{RT}{F} \ln(K_I c_A) + \frac{RT}{2F} g + E^\circ \quad (4-5)$$

and

* This simply provides a basis of reference for expressing coverages and currents as a function of potential, and in the irreversible case, for expressing peak potentials on a relative scale.

$$i_p = \frac{QFs}{RT(4+g)} \quad (4-6)$$

respectively. Also

$$C_p = \frac{OF}{RT(4+g)} \quad (4-7)$$

The eqn. (4-7) corresponds to the maximum adsorption pseudocapacitance C given by $C_p = \frac{i_p}{s}$, previously evaluated^{31,32}.

The irreversible case involves only one main term of eqn. (4-1) depending whether a deposition or film-stripping process is involved. The case where the rate equation [eqn. (4-1)] can be written

$$i = Q \frac{d\theta_B}{dt} = Q k_1' c_A (1-\theta_B) \exp\left[\frac{\Delta V}{b} - (1-\beta)g\theta_B\right] \quad (4-8)$$

is considered. Differentiating this equation with respect to time t to obtain i_p and V_p and noting that the current will be a maximum when

$$\frac{d\theta_B}{dt} = \frac{(1-\theta_B) s/b}{1 + (1-\beta)g(1-\theta_B)} , \quad (4-9)$$

i.e., for the condition $\frac{di}{dt} = 0$, it is found that

$$i_p = \frac{Qs}{b} \frac{(1-\theta_{B,p})}{1 + (1-\beta)g(1-\theta_{B,p})} \quad (4-10)$$

where $\theta_{B,p}$ is the coverage at the peak potential. The potential V_p corresponding to i_p is obtained from eqns. (4-8) and (4-10) as

$$V_p = b \ln \frac{s}{k_1 b} - b \ln [1 + (1-\beta)g(1-\theta_{B,p})] + b(1-\beta)g\theta_{B,p} + E^\circ \quad (4-11)$$

where

$$k_1 = k_1' c_A \quad (4-12)^*$$

An expression for $\theta_{B,p}$, which can only be evaluated numerically by an iterative method, is

$$\theta_{B,p} = 1 - \exp\left\{-\frac{\exp[-(1-\beta)g(1-\theta_{B,p})]}{1 + (1-\beta)g(1-\theta_{B,p})} - \sum_{n=1}^{\infty} \frac{[-(1-\beta)g]^n}{n \cdot n!} [(1-\theta_{B,p})^{n-1}]\right\} \quad (4-13)$$

the derivation of which is given in Appendix II. Eqn. (4-13) was used to check the value of $\theta_{B,p}$ obtained from the numerically integrated eqn. (4-1). Comparisons were satisfactory for $g \leq 10$ but for $g > 10$, convergence problems arise in the iterative evaluation of $\theta_{B,p}$ from eqn. (4-13).

For the Langmuir case, $g = 0$, $\theta_{B,p}$ reduces to the simple result

$$\theta_{B,p} = 1 - \exp(-1) = 0.63 \quad (4-14)$$

obtained by Srinivasan and Gileadi⁹⁰ for an irreversible 1-e electro-sorption process under Langmuir conditions.

The current maximum i_p and the potential V_p at which it occurs are obtained by substituting $\theta_{B,p}$ from eqn. (4-13) into eqns. (4-10) and (4-11), respectively.

* For reactions such as (I), which are driven by a linear potential sweep, s/k' would have the units of $V \text{ mol l}^{-1}$ taking c_A in mol l^{-1} . Since in all the calculations, c_A was taken for convenience as 1, $k_1' c_A$ will be written as k_1 where k_1 is another constant equal in magnitude to $k_1' c_A$ when c_A is unity. It is convenient to include this "standard" concentration with k_1' whenever appropriate so that k_1 and k_{-1} then have the same units (sec^{-1} , noting that Q is a charge per cm^2) and s/k for both the backward and forward directions of the process then have the same significance and the same units (V).

Derivation of an equation, which proves that the C-V profiles for the irreversible 1-e electrochemical surface reaction under Langmuir conditions, i.e., $g = 0$, are identical in form and independent of the sweep-rate s [so long as the process remains irreversible, i.e., (see below) when $s > s_0$, the limiting sweep-rate for reversible behaviour] and V_p value, is given in Appendix III.

4.4 Current-Potential Profiles for the 1-e Surface Reaction when Lateral Interactions are Absent ($g = 0$)

Solution of eqn. (4-1) for absence of lateral interactions, $g = 0$, i.e., for Langmuir conditions in eqn. (4-3), gives rise to the familiar i-V profiles shown in Fig. 4-1 (cf. ref. 90), which for reasons of convenience are represented as usual (cf. refs. 31,32,90) in terms of the adsorption pseudocapacitance $C(= \frac{i}{s} = \frac{Q}{s} \frac{d\theta_B}{dt})$ as a function of potential.

While the form of such profiles is well-known^{31,56,80,90,93}, it may be useful to emphasize that the peaked shape of these current-potential relations arises from the opposing tendencies for the reaction to exponentially increase its rate as potential is raised but be decreased in rate as the free-surface $1-\theta_B$ decreases as the coverage of B increases towards a monolayer [$1-\theta_B$ factor in eqn. (4-1)]. A similar argument can be made for the reverse direction of (I) as the coverage of B becomes zero at sufficiently large potentials in the opposite direction.

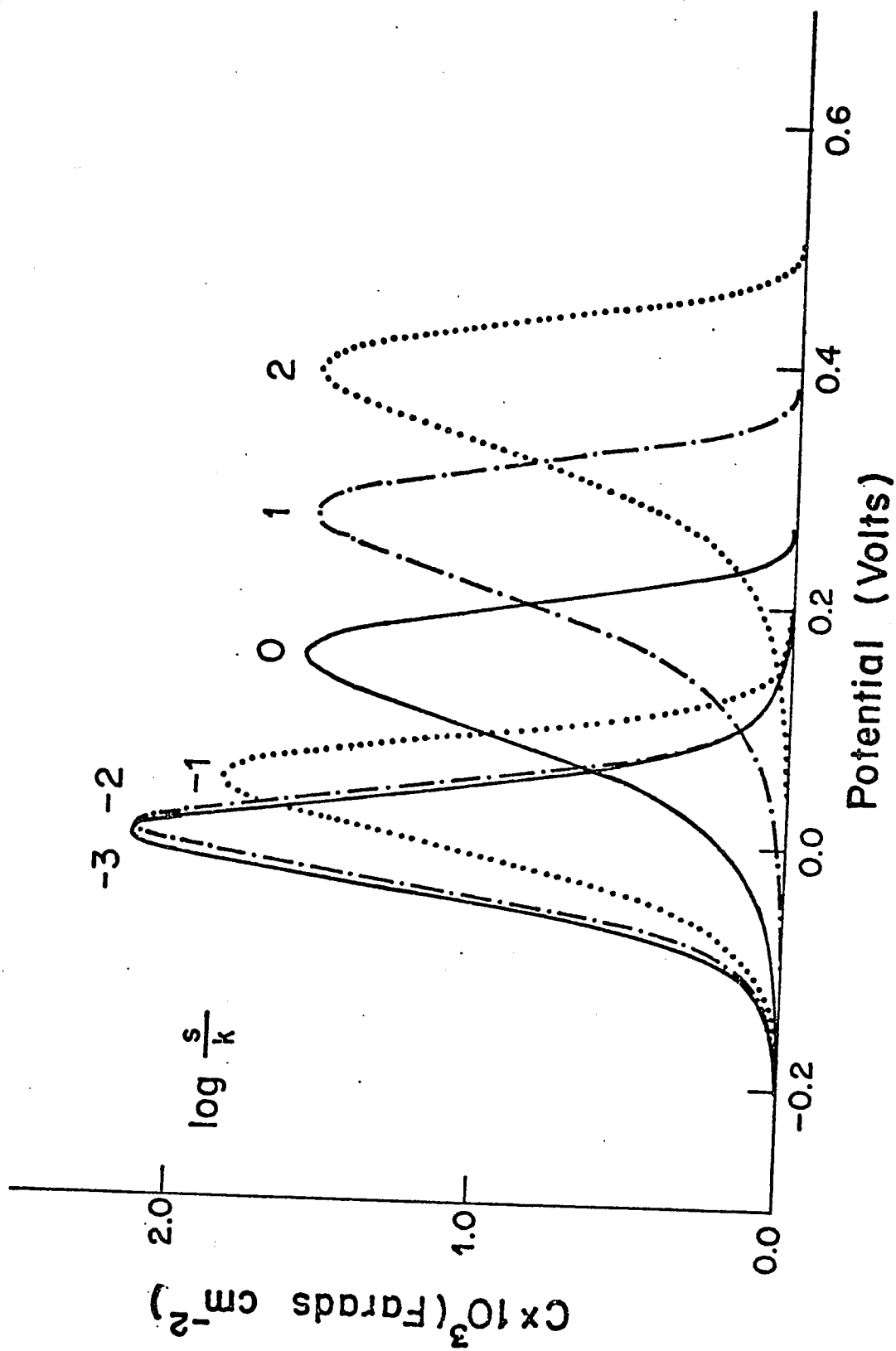


Fig. 4-1 Series of C vs. V profiles for reaction (I) for various s/k values showing progression from reversible to irreversible behaviour when parameter $g = 0$ (cf. ref. 90).

Generalized plots of the kinetics can be given by relating the C vs. V behaviour to a reduced sweep-rate s/k^* . Then for reactions such as (I) having any rate constant k , a common behaviour can be represented. For convenience, in order to avoid overlap of the C - V profiles, those for the cathodic-going sweep would be plotted in a 180° rotated position, i.e., below the potential axis in the figures to be shown below and in other chapters as well, i.e., as they would be recorded in measurements of current, i.

As can be seen from the results of the computer calculations and from Fig. 4-1, the electrochemical surface reaction (I) is reversible for $\frac{s}{k} \leq 10^{-2}$. Practically, it can be considered totally irreversible from $\frac{s}{k} > 1$.

The main quantities characterizing the behaviour shown in Fig. 4-1 are plotted in Fig. 4-2 as a function of reduced sweep-rate, $\log \frac{s}{k}$; the characteristic parameters are (a) the peak potential V_p , (b) the peak pseudocapacitance C_p and (c) the half-width $\Delta V_{1/2}$, i.e., the potential span across the curve at half the peak current⁹³. As can be seen, the plot of V_p vs. $\log \frac{s}{k}$ (Fig. 4-2) is equivalent to a Tafel relation for the surface process¹⁰⁴ with a slope equal to the Tafel slope 2.3b.

As will be shown in a forthcoming paper¹⁴², this gives a useful way of characterizing the reversibility of a surface process

* In the graphical representation of the results, the kinetic behaviour is shown as a function of s/k values which are equivalent either to s/k_1 or s/k_{-1} (see eqn. (4-12) and its footnote).

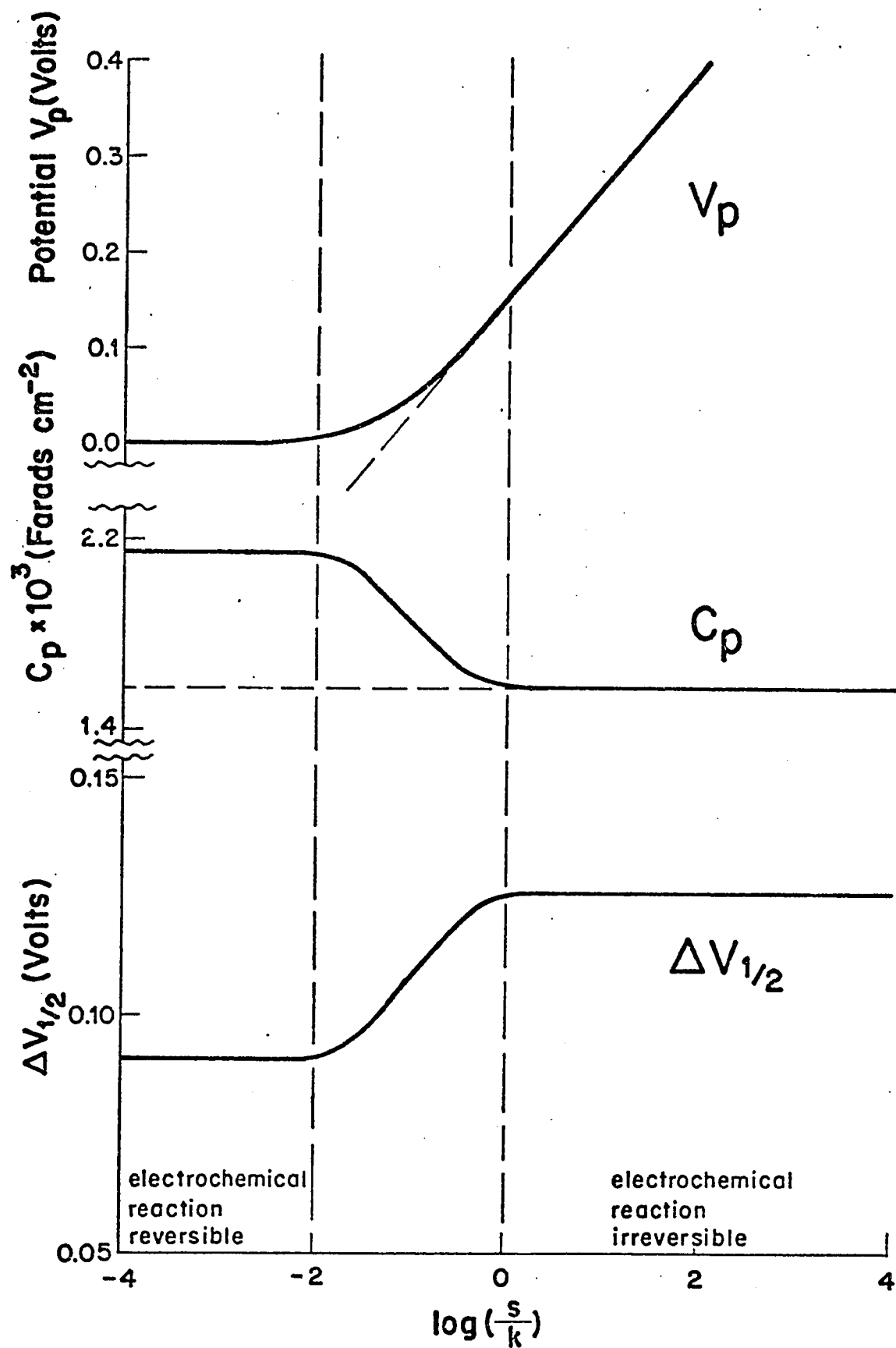


Fig. 4-2 Plots of V_p , C_p and $\Delta V_{1/2}$ values from Fig. 4-1 vs. $\log \frac{s}{k}$ showing the transition from reversible to irreversible behaviour. The interaction parameter $g = 0$.

by extrapolating a plot of V_p vs. $\log s$ to the reversible potential for the process and thus deriving an extrapolated sweep-rate, s_o , which is analogous to an exchange current density, i_o . Correspondingly C_p can be plotted (Fig. 4-2) against $\log \frac{s}{k}$ illustrating the transition from reversible to irreversible behaviour in Fig. 4-1 for reaction (I) as $\frac{s}{k}$ increases⁹⁰. The peak C values decrease towards a limiting value as $\frac{s}{k}$ is increased while the C-V curves of Fig. 4-1 become asymmetrical in shape with V_p occurring at $\theta_B (= \theta_{B,p}) = 0.63$ instead of at 0.5 as for the reversible case. The change of shape of the peak with increasing $\frac{s}{k}$ is reflected (cf. ref. 93) in the change of $\Delta V_{1/2}$ value (Fig. 4-2) which, for the limiting cases of reversible and totally irreversible conditions, assumes, as C also does, two different constant values.

It is useful to mention here that when reaction (I) is completely reversible, the cathodic sweep is a mirror image of the anodic one throughout the C vs. V profile, i.e., at all values of θ_B (Fig. 4-3a). With increasing s, as the process is driven more irreversibly, the peaks shift in the direction of the sweep: anodic to more positive potentials, cathodic to more negative potentials and an increasing separation between the peaks for the forward and backward directions develops (Fig. 4-1 and Figs. 4-3a-d below). The development of irreversibility can also be seen when the direction of sweep is reversed prior to completion of the monolayer in the forward anodic sweep direction; then (Figs. 4-3b,c) the current does not immediately change to that for the cathodic overall C-V profile corresponding to reduction

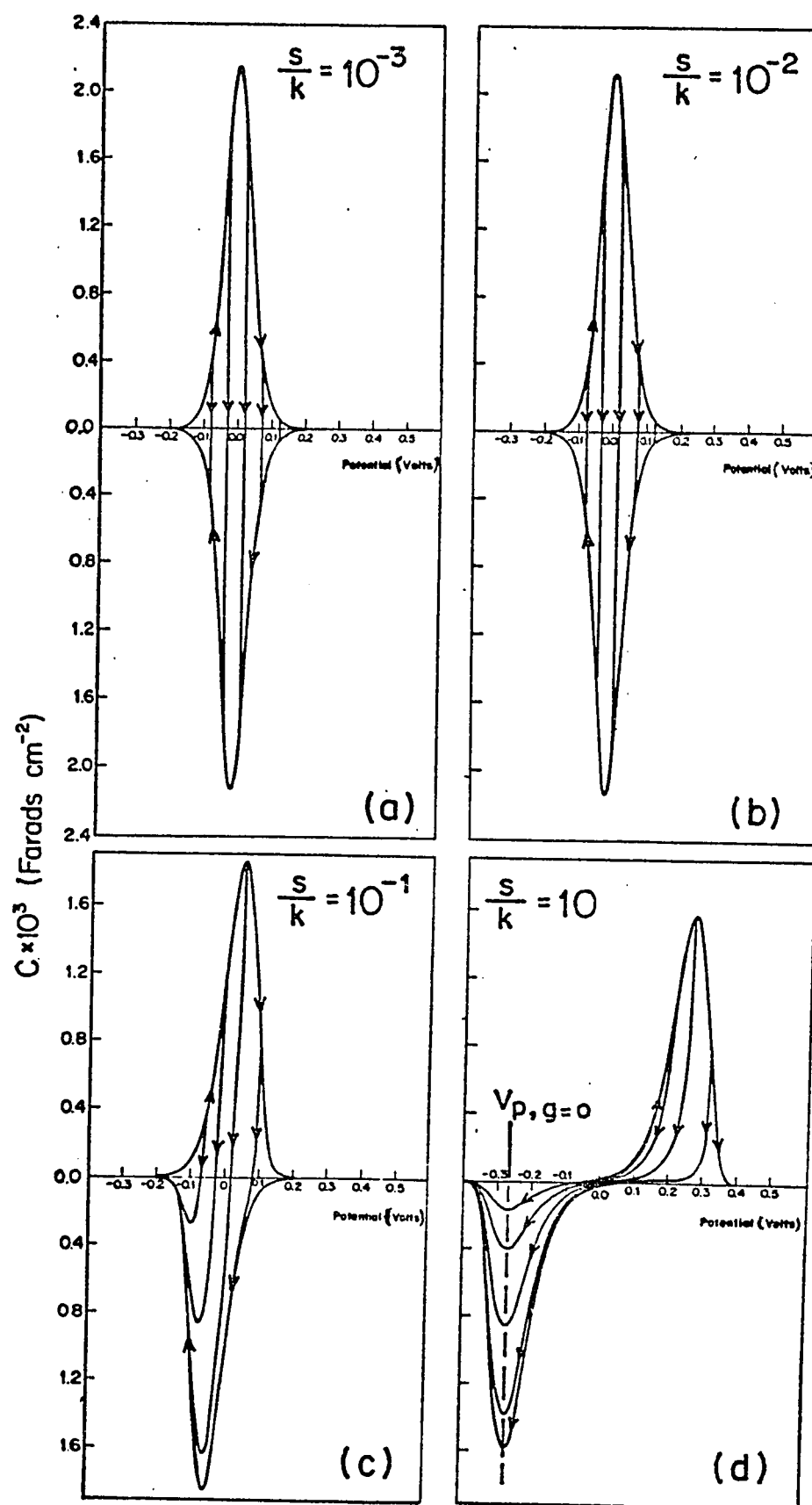


Fig. 4-3 Anodic and cathodic C-V profiles for various initial cathodic θ_B values and for various degrees of reversibility of reaction (I). The values of s/k are: (a) 10^{-3} , (b) 10^{-2} , (c) 10^{-1} , (d) 10 and $g = 0$ in all cases.

of the complete monolayer, $\theta_B = 1$, so that a lag develops in the reversed C vs. V profile until, in the completely irreversible case, a series of displaced independent reverse current profiles are generated (Fig. 4-3d). It was shown in previous experimental work^{61,74} how this behaviour is useful for distinguishing the response of co-adsorbed H and acetonitrile on Pt in terms of their kinetic relaxation characteristics and for deriving their relative extents of coverage on the electrode. This will be discussed in more detail in Chapter V. Similar applications were made⁷⁴ to distinction of reversible and irreversible species in Pt surface oxidation.

An important feature of the family of curves in Fig. 4-3d is that the C vs. V profiles generated on the reverse sweep all have identical shapes and thus the same $\Delta V_{1/2}$ values, and have their maxima at the same potential, V_p . This is simply a consequence of reduction of different quantities, θ_B , of B generated in the preceding forward sweep taken to different potentials as shown in Fig. 4-3d. The profiles are all determined by the same function (eqn. (4-1) with $g = 0$) (cf. ref. 31) and only differ by a scaling factor determined by the Q value which, for the series of reverse sweep curves is given by Q for the monolayer times the values of θ_B attained at the potential at which the reduction begins on the reversed sweep.

A summary of the characteristic parameters for the kinetics of the l-e surface reaction for $g = 0$ is given in Table 4-1. Experimental verification of these characteristic features, e.g., V_p vs. $\log s$ plots, the change of i_p/s with $\log s$ and the half-width, $\Delta V_{1/2}$, was recently made experimentally by Kozłowska and Conway¹⁴² for one of the states of H adsorption at Pt.

Table 4-1. Characteristic Quantities for Reaction (I) ($g = 0$ for the adsorbed layer of B) under Potential-Sweep Conditions

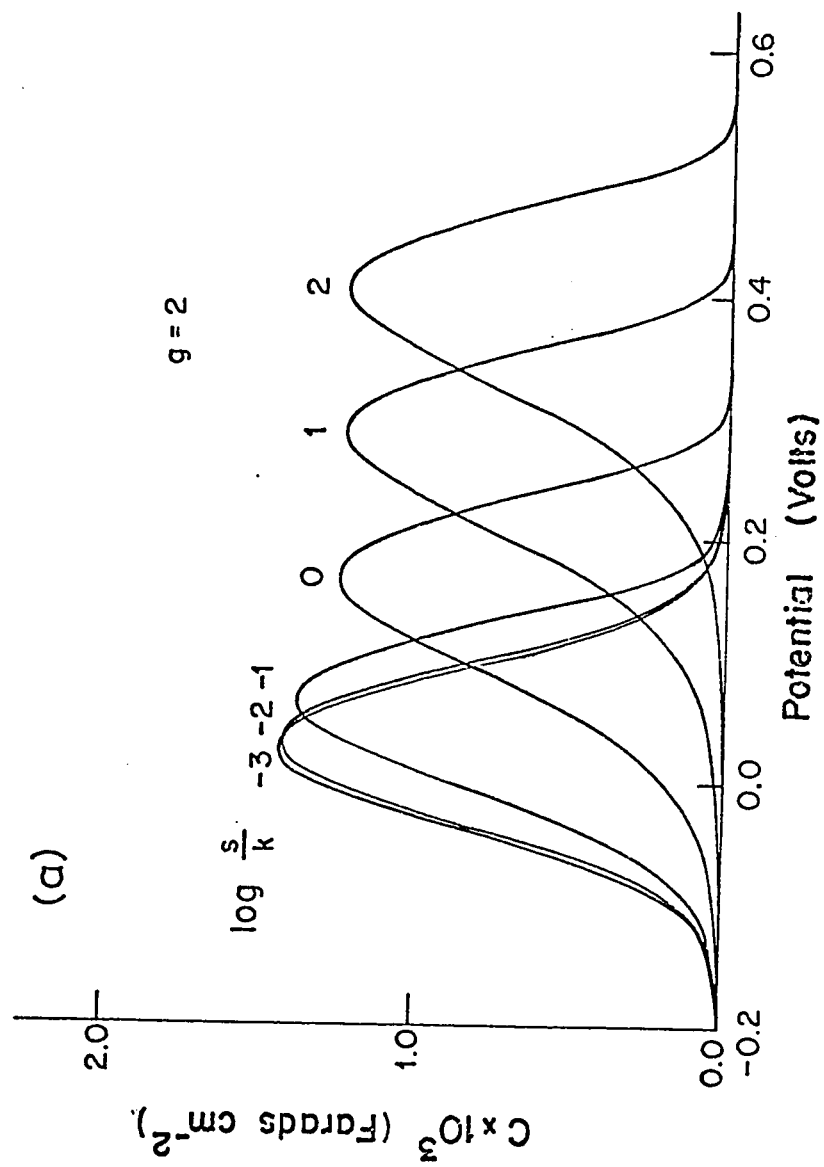
Parameters	$C_p (=i_p/s)$ (Farad cm^{-2})	$\Delta V_{1/2}$ (V)	$\theta_{B,p}$	$dV_p/d \log \frac{s}{k}$ (V)
Value for reversible conditions	2.14×10^{-3}	0.091	0.50	0
Value for irreversible conditions	1.57×10^{-3}	0.126	0.63	0.118

4.5 Effects of Lateral Interactions ($g \neq 0$) in the Chemisorbed Layer

The existence of lateral interactions between the chemisorbed species on the surface, i.e., for $g \neq 0$ in the isotherm [eqn. (4-3)], has the effect of changing the aspect-ratio of the C vs. V profiles, making them lower and broader as $g > 0$ or sharper and taller as $-4 < g < 0$ (a singularity arises at $g = -4$ in eqn. (4-3), corresponding to two-dimensional phase separation⁵⁶). Figs. 4-4a,b show C vs. V profiles for reaction (I) at various s/k values when $g \neq 0$; behaviour for $g = -2$ and $+2$ is plotted which is to be compared with that shown in Fig. 4-1 for $g = 0$. A series of C vs. V profiles which arise for various values of g when reaction (I) is behaving reversibly or irreversibly are shown in Figs. 4-5a and b, respectively. The electrochemisorption isotherms, corresponding to various values of g in eqn. (4-3) and to the profiles in Fig. 4-5a, are shown in Fig. 4-6, together with the imaginary case for a g value < -4 (cf. ref. 56). The C as $f(V)$ profiles for the equilibrium case (Fig. 4-5a) are, of course, the differential coefficients of these curves with respect to V.

Fig. 4-4 (a) C-V profiles for reaction (I), when the interaction parameter $g = 2$, calculated for various s/k values showing progression from reversible to irreversible behaviour.

(b) As in (a) but for $g = -2$



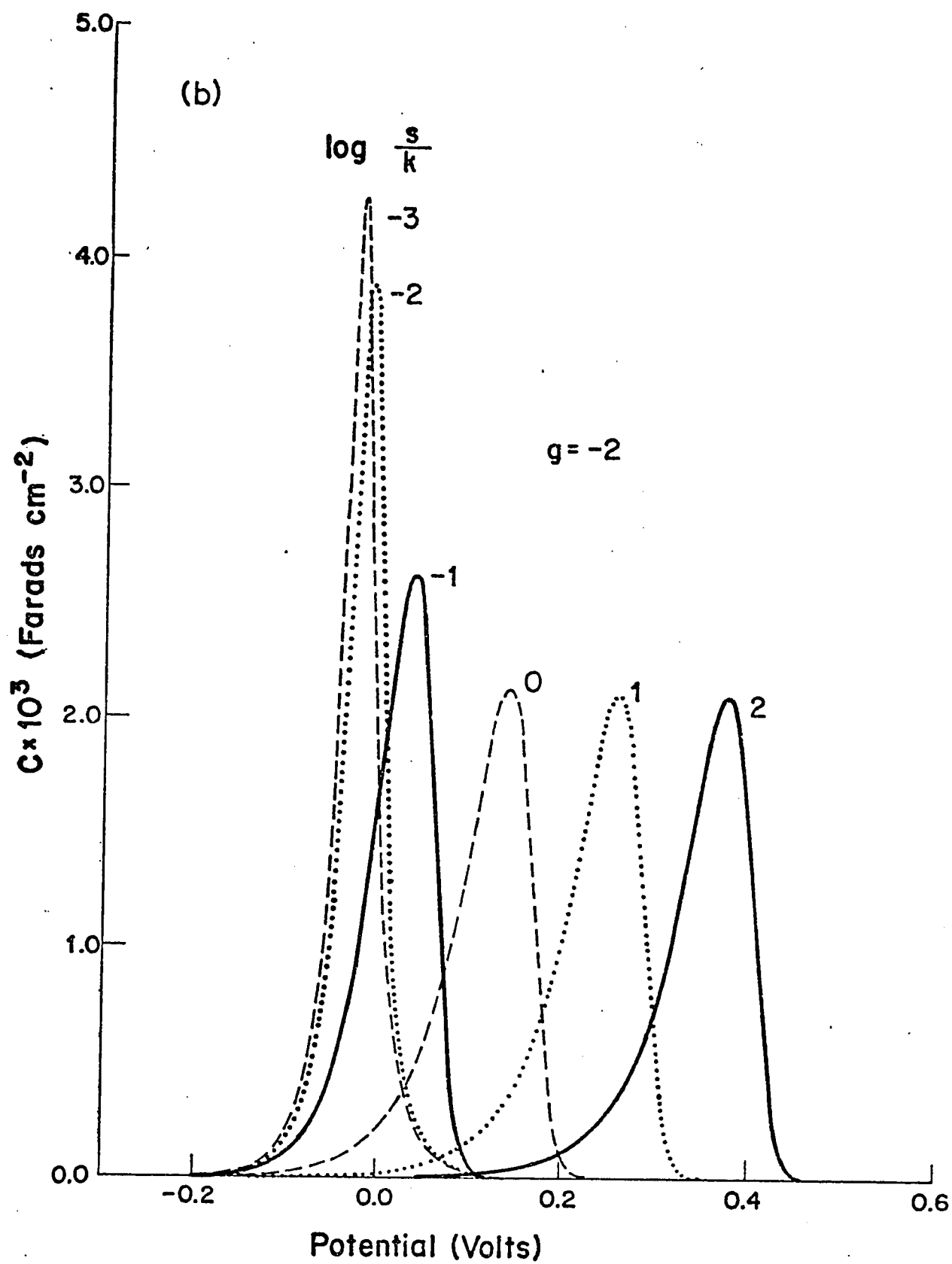
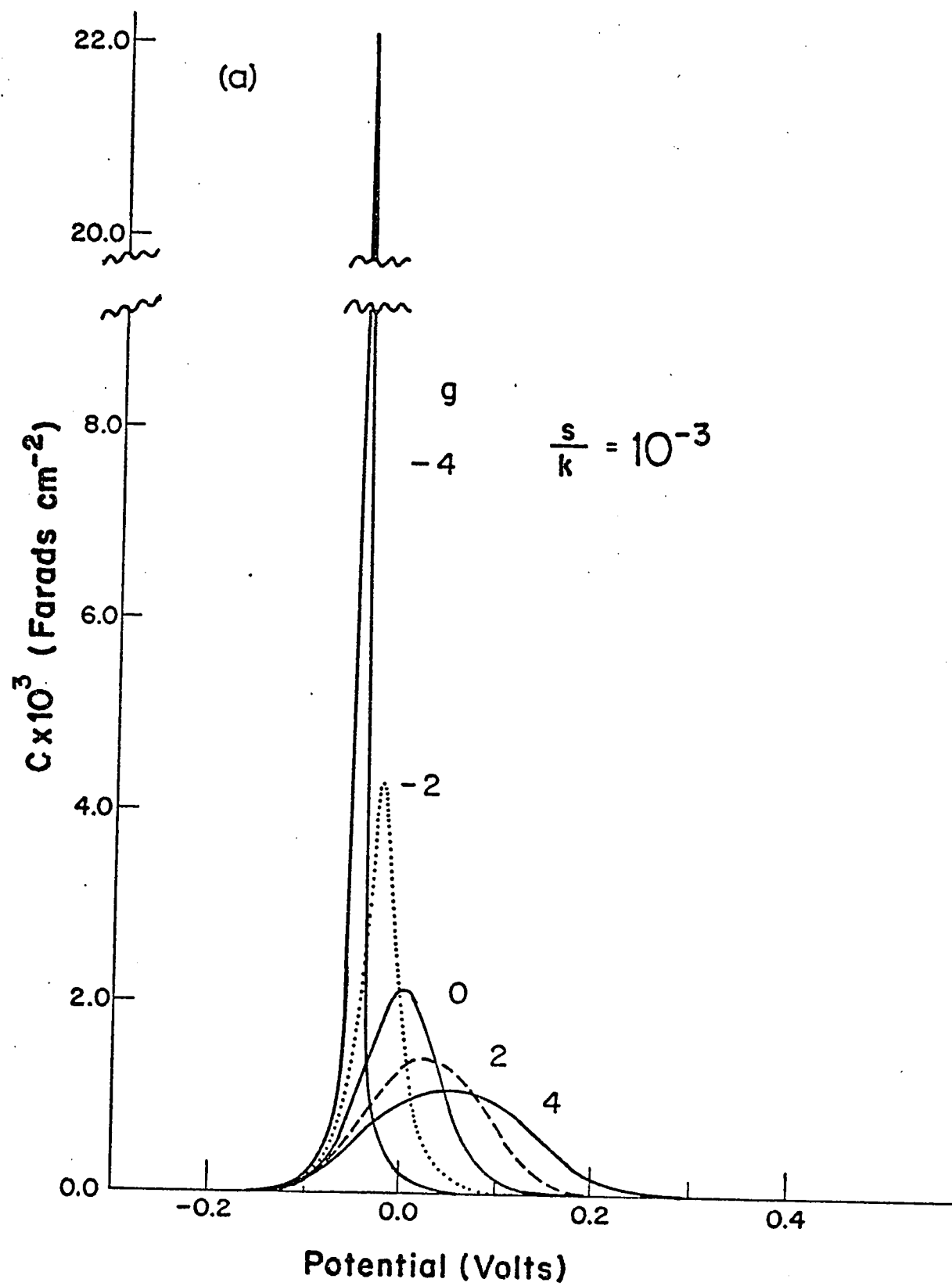
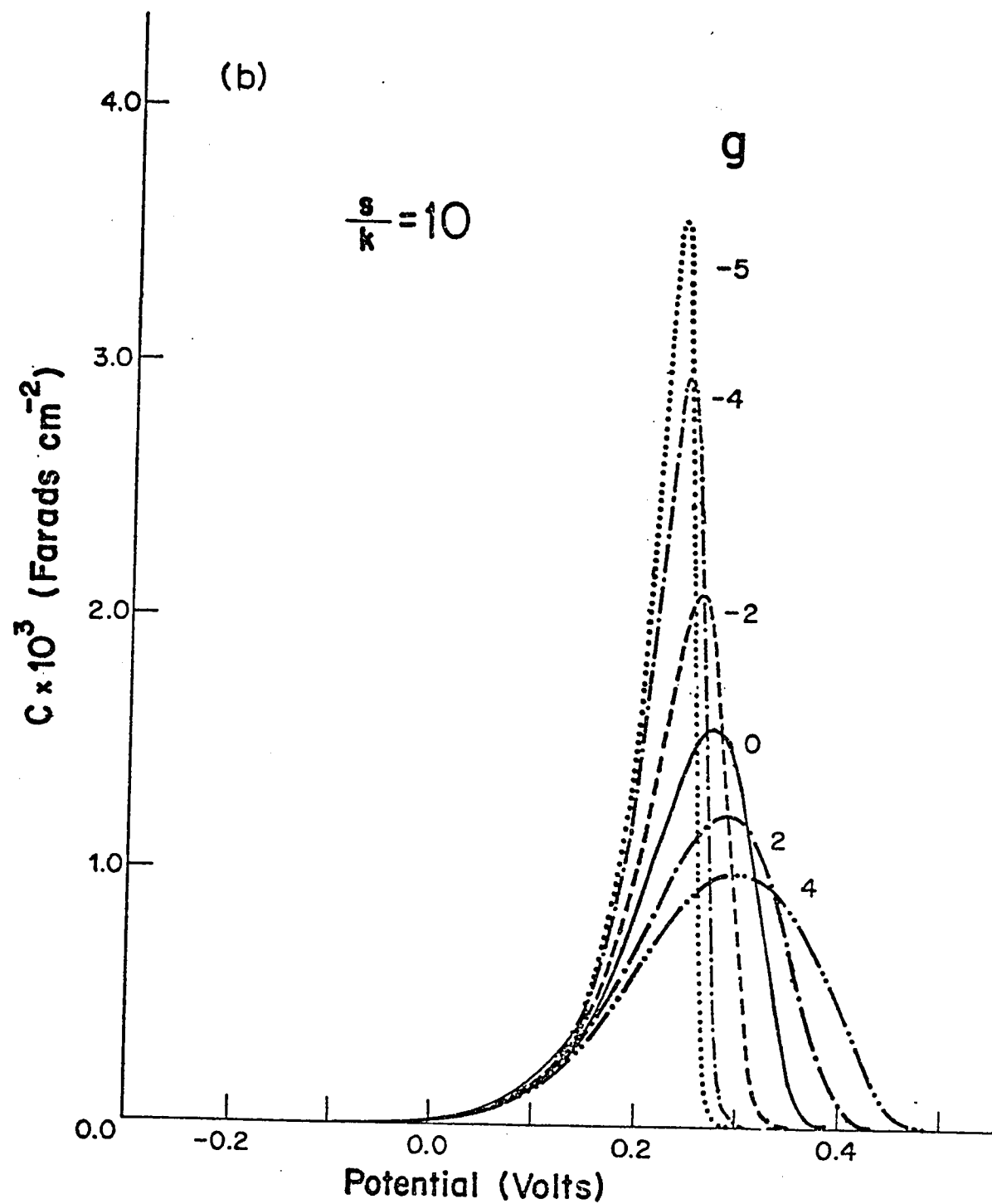


Fig. 4-5 Plots of the C vs. V profiles for reaction (I)
for various positive and negative g values in
eqn. (4-1).
(a) For reversible conditions;
(b) For irreversible conditions.





The dependence of the peak pseudocapacitance on the reduced sweep-rate, $\log \frac{s}{k}$, can also be observed from Figs. 4-4a,b for $g = +2$ and -2 , respectively. It can be seen that the change in C_p is more pronounced for negative g values (cf. Fig. 4-4b) than for positive ones (cf. Fig. 4-4a) as a function of $\log \frac{s}{k}$ when going from reversible to irreversible profiles (cf. Fig. 4-2). As $g \rightarrow 10$, it could be demonstrated that the value of C_p for the reversible process tends to become equal to that for the irreversible process, i.e., C_p is almost independent of $\log \frac{s}{k}$. On the other hand, as $g \rightarrow -4$, the difference between reversible and irreversible C_p values increases more and more.

$\Delta V_{1/2}$ as a function of g , for positive and negative g values, is shown in Fig. 4-7, together with other characteristic parameters of the C vs. V profiles for reaction (I), such as the coverage $\theta_{B,p}$ of B at the peak and the peak potential V_p . Fig. 4-7 also shows the standard-state coverage, θ° , as a function of g . As discussed by Conway, Angerstein-Kozłowska and Dhar³⁰, for $g \neq 0$, θ° no longer corresponds to the maximum in the C vs. V profile but to the standard electrode potential E° defined³⁰ for all g values as the peak potential for reaction (I) behaving reversibly with no lateral interactions ($g = 0$). θ° enables E° to be found from experimental C - V profiles when $g \neq 0$.

As a basis for characterizing the interactions in the surface layer, the most useful diagnostic parameter is (cf. ref. 93) the $\Delta V_{1/2}$ value. The value and sign of g are required for two reasons:

- (a) for calculating the kinetic parameters of the surface reaction through eqn. (4-1) or by means of a plot of V_p vs. $\log \frac{s}{k}$ giving s_o ¹⁴²;

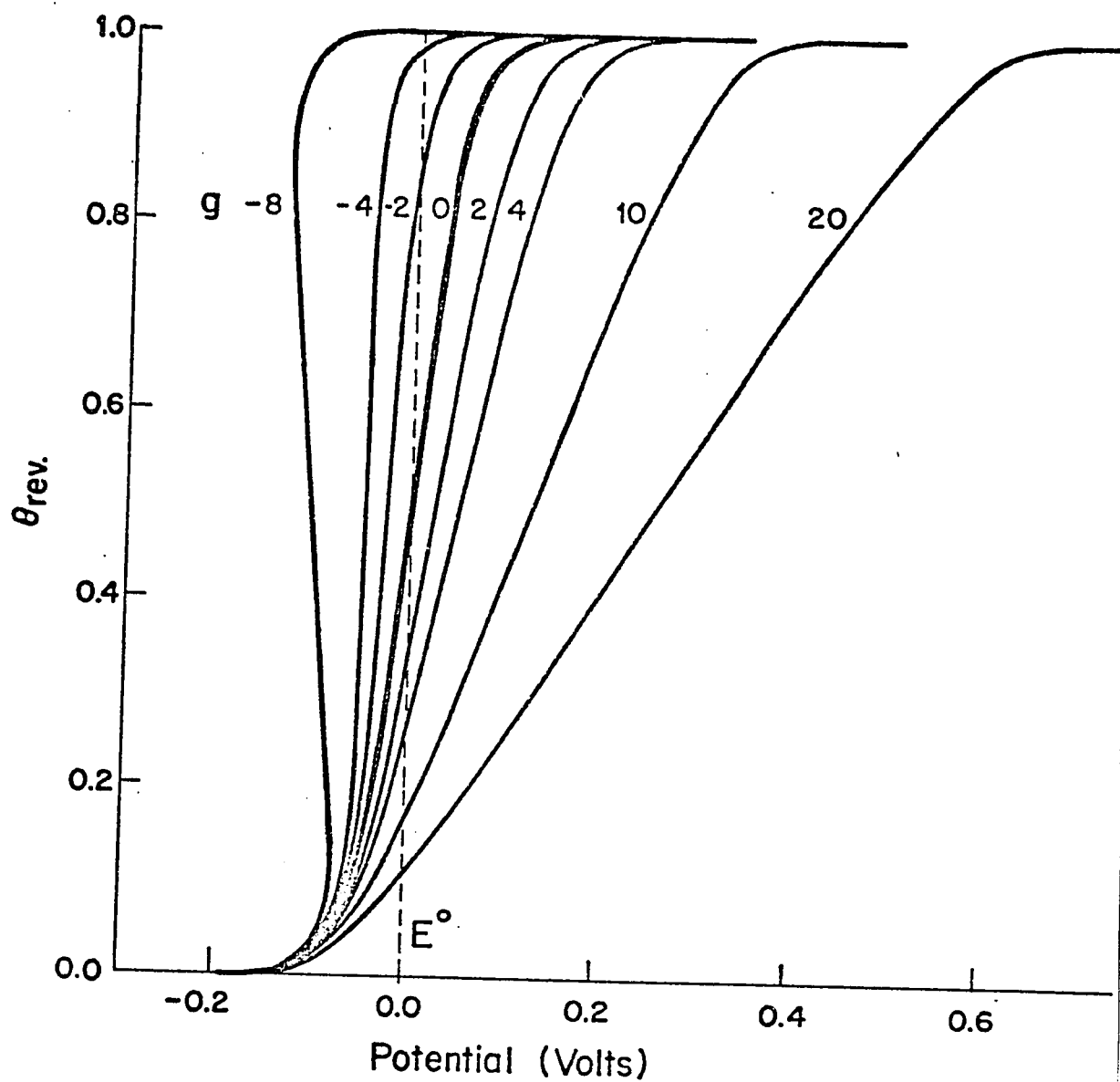


Fig. 4-6 Adsorption isotherms for species B in reaction (I) for various positive and negative g values, including a hypothetical case of $g = -8$.

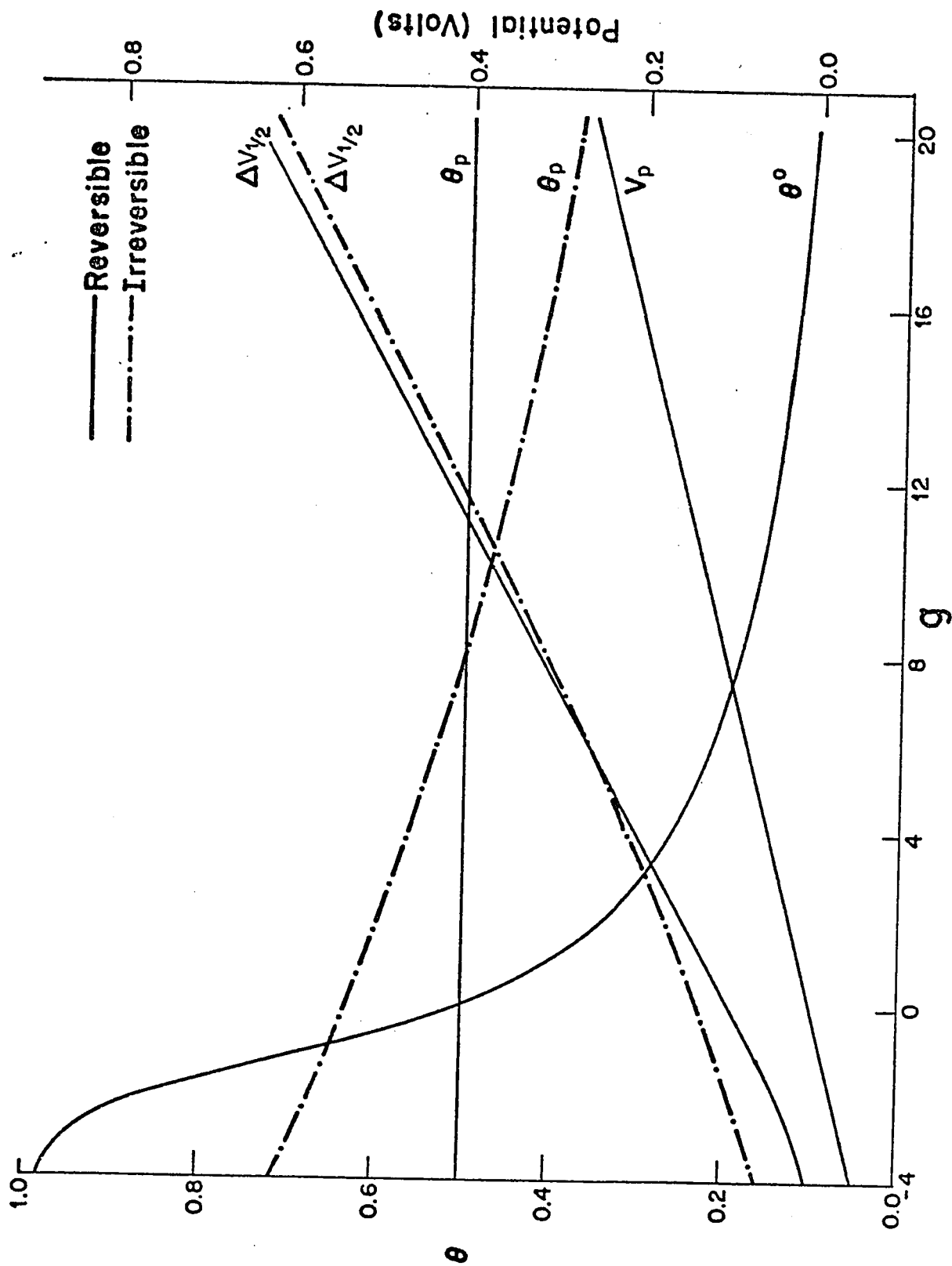


Fig. 4-7 Dependence of parameters V_p , θ_p , $\Delta V_{1/2}$ and θ° , characterizing the C-V profiles for reversible and irreversible conditions in reaction (I), on the value of g .

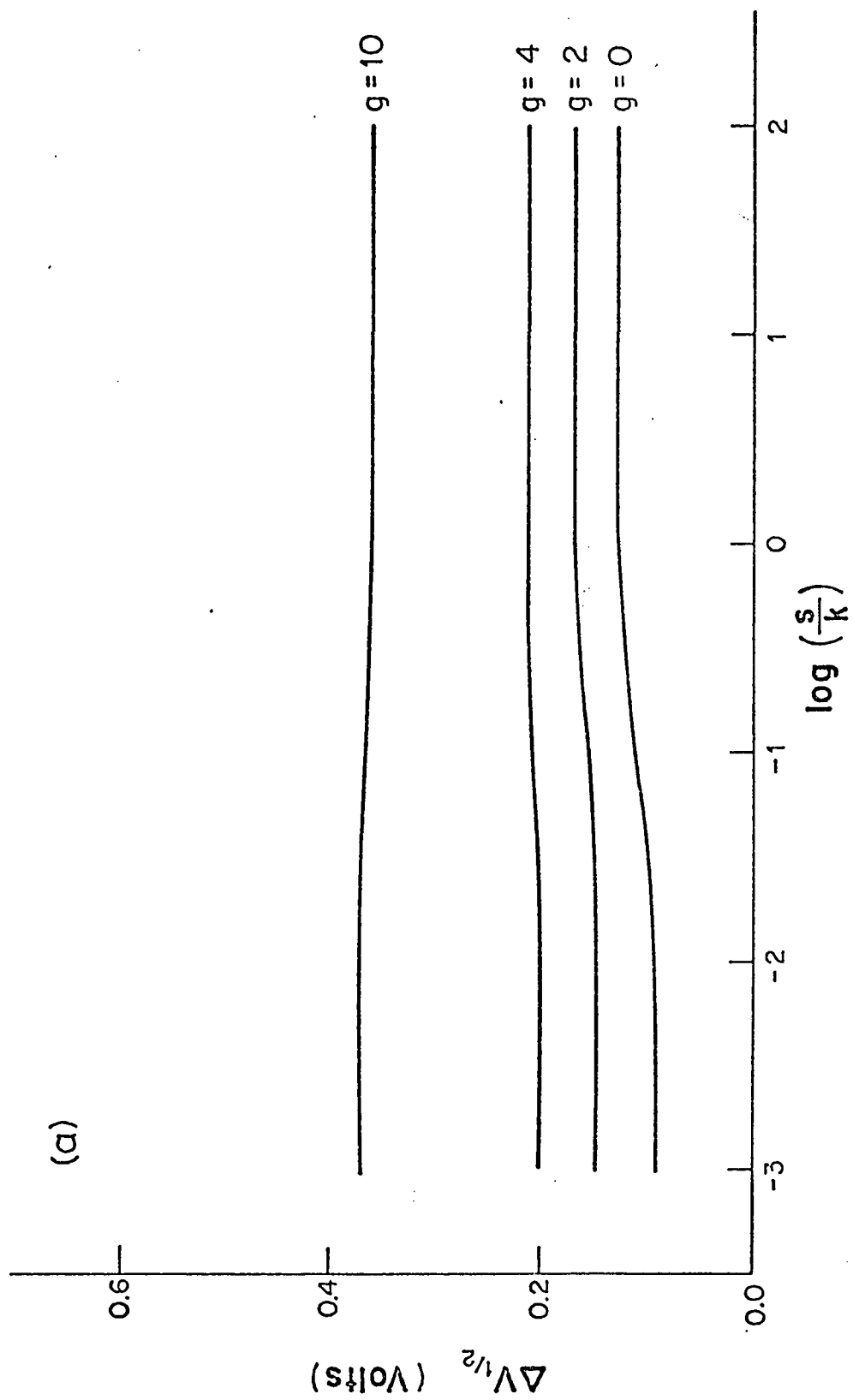
and

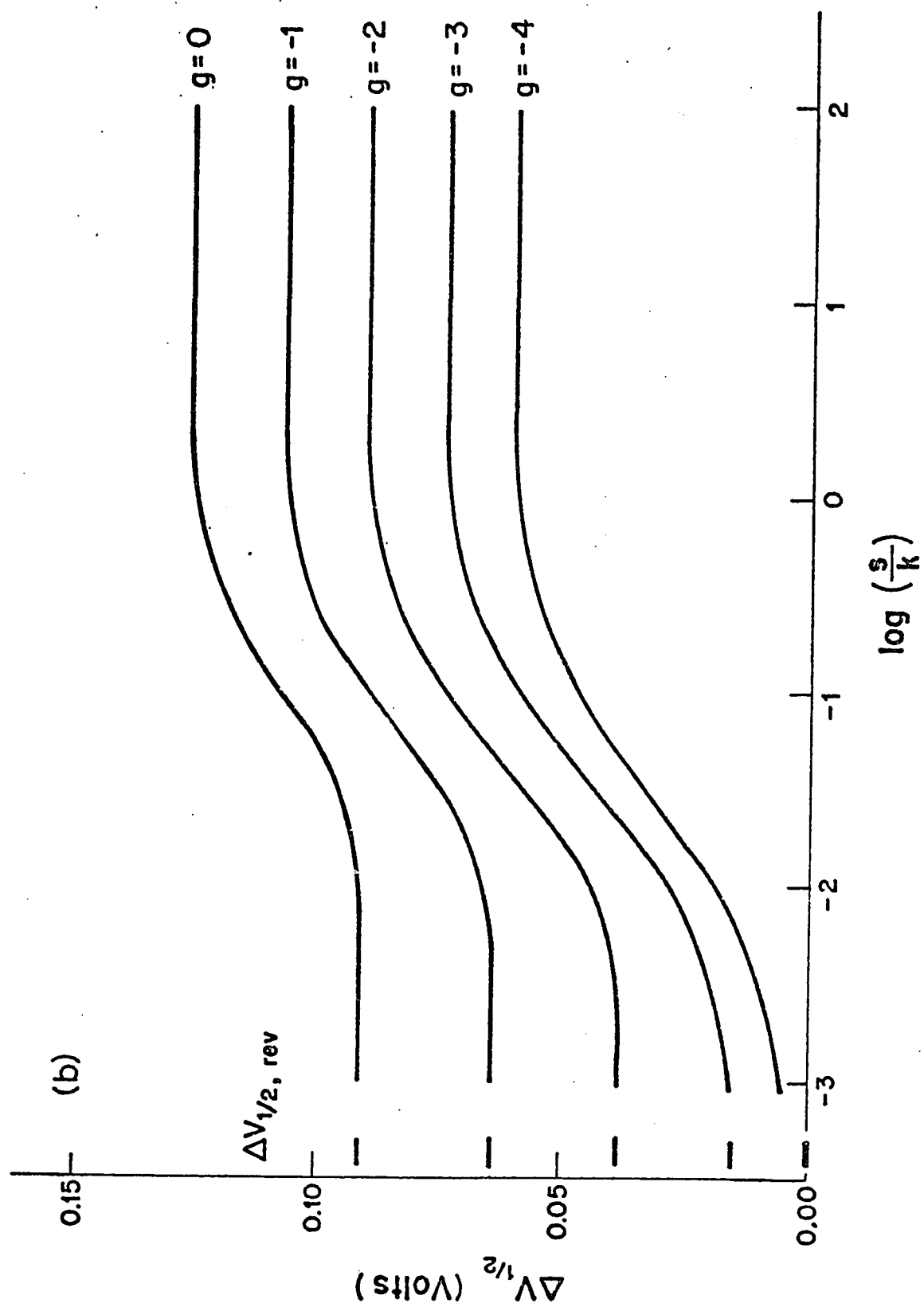
(b) for indicating the electrical state of chemisorbed species.

Thus the observed $\Delta V_{1/2}$ values for the H adsorption peaks at Pt require zero or small negative values of g which must indicate that the adsorbed H is not significantly charged. Also, underpotential deposited Pb species on Au with appreciable ionic character, as proposed in ref. 143, are ruled out¹⁴⁴ because the observed well resolved multiple peak structure in the i/s vs. V profile would not arise if even a small positive value of g due to coulombic repulsion in the adsorbed Pb atom layer would exist. Thus, positive g would give rise to much broader and lower C peaks with consequently more overlap than is observed.

Not only does the value of g determine the half-width of reversible and irreversible C vs. V profiles (Figs. 4-7) but it has an important effect on the relative values of C_p as the transition from reversible to irreversible behaviour in reaction (I) occurs with increasing s/k . This may be shown in two ways: (a) by comparing the C vs. V profiles of Figs. 4-4a,b for $g = -2$ or $+2$ with those of Fig. 4-1 for $g = 0$ and (b) by plotting $\Delta V_{1/2}$ vs. $\log \frac{s}{k}$ for various positive (Fig. 4-8a) or negative values of g (Fig. 4-8b). For the positive values of g , $\Delta V_{1/2}$ increases with s/k but the effect diminishes with increasing g until, when g approaches 10, little variation remains. For $-4 < g \leq 0$, on the other hand, $\Delta V_{1/2}$ increases relatively more strongly and near to -4 continues to vary with $\log \frac{s}{k}$ over a much wider range than for the case, e.g., when $g = 0$. This is actually observed experimentally for the spike in the C vs. V profile for Pb atom deposition and ionization at Au⁶⁴.

- Fig. 4-8 (a) Dependence of $\Delta V_{1/2}$ on $\log \frac{s}{k}$ for various positive values of g in reaction (I).
- (b) As in (a) but for various negative values of g in reaction (I).





For sufficiently high s values ($s > s_0$), all surface processes will behave irreversibly. Then a Tafel type behaviour will be observed for the currents or peak currents as a function of potential of a given coverage in the sweep. It is convenient to express peak currents in terms of s and relate $\log s$ to V_p . A Tafel relation is then derived for the surface process and characterizes its kinetics, the Tafel slope being $dV_p/d \log s$.

The relative change of peak potential, V_p , with $\log \frac{s}{k}$ for various positive and negative values of g is shown in Fig. 4-9. As in Fig. 4-8b, it is to be noted that as g is changed from -4, through 0, to appreciable positive values (Fig. 4-8a), the transition region for variation of V_p with $\log \frac{s}{k}$ from reversible to irreversible conditions becomes narrower. For negative g , the reversible behaviour is approached only over a wide range of $\log \frac{s}{k}$ values.

The Tafel plots for the surface process are also of interest in relation to values of $g \neq 0$. As discussed in a recent experimental paper¹⁴⁵ for the case of surface film reduction, it is convenient to write the pseudocapacitance as $\log \frac{i/s}{1-\theta_B}$ [cf. eqn. (4-8)] and then plot potential V as a function of $\log \frac{i/s}{1-\theta_B}$. In the film stripping case this independent variable would be written¹⁴⁵ $\log \frac{i/s}{\theta_B}$. Fig. 4-10 shows the Tafel-type relations for $g = 0, 4$ and 10 for an irreversible 1-e electrochemical surface process involving deposition of an ad-species; an s/k value of 100 was taken. Beyond $\log \frac{i/s}{1-\theta_B} = -5$, θ_B becomes greater than 0.01 (the lower limit of experimentally measurable θ_B values) and deviations from linearity of the Tafel-type plots set in

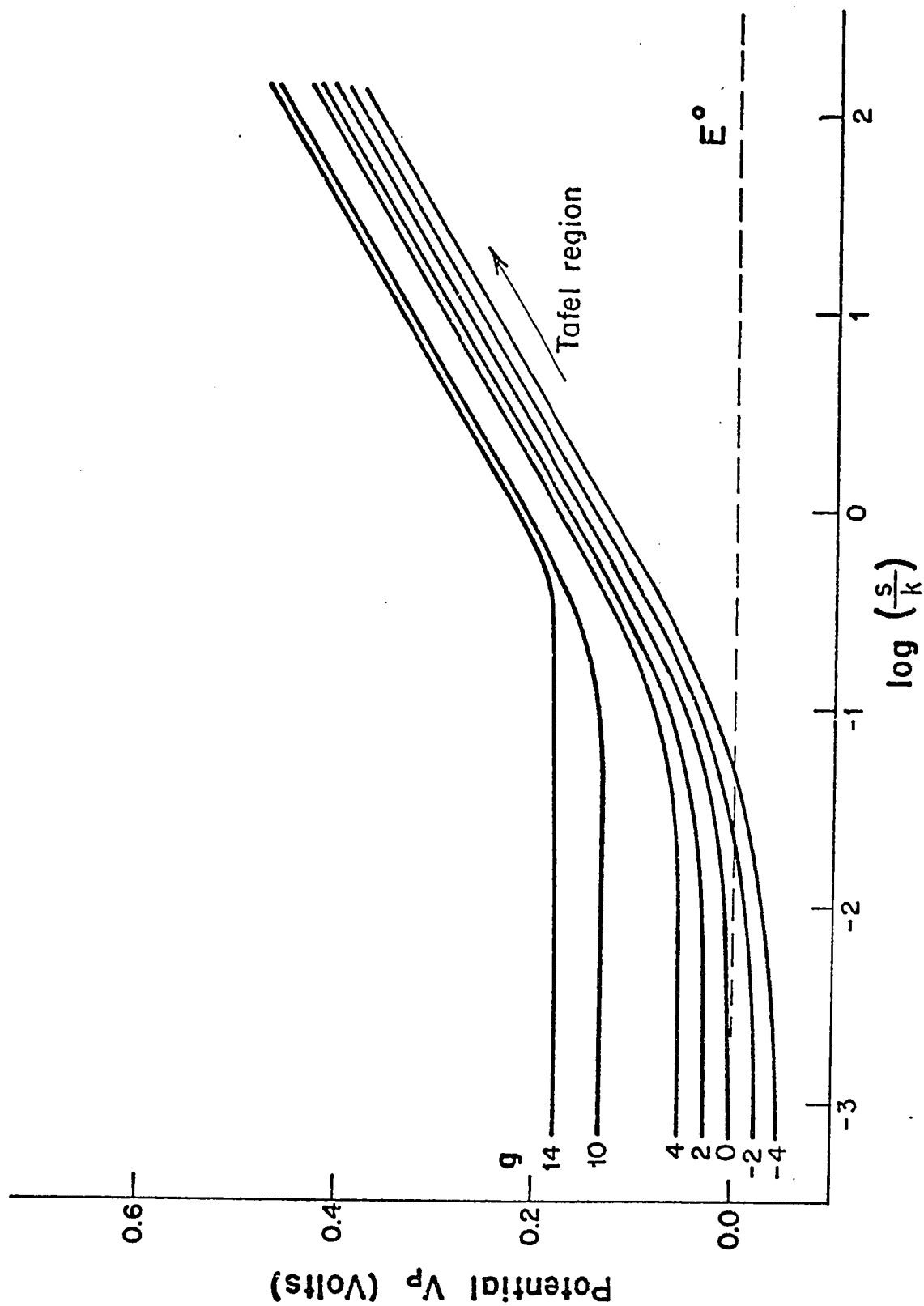


Fig. 4-9 Plots of V_p vs. $\log \frac{s}{k}$ showing how transition from reversible (low s/k values) to irreversible (high s/k values) behaviour depends on the value of g . V_p values are referred to $E^\circ = 0.0$ V indicated by

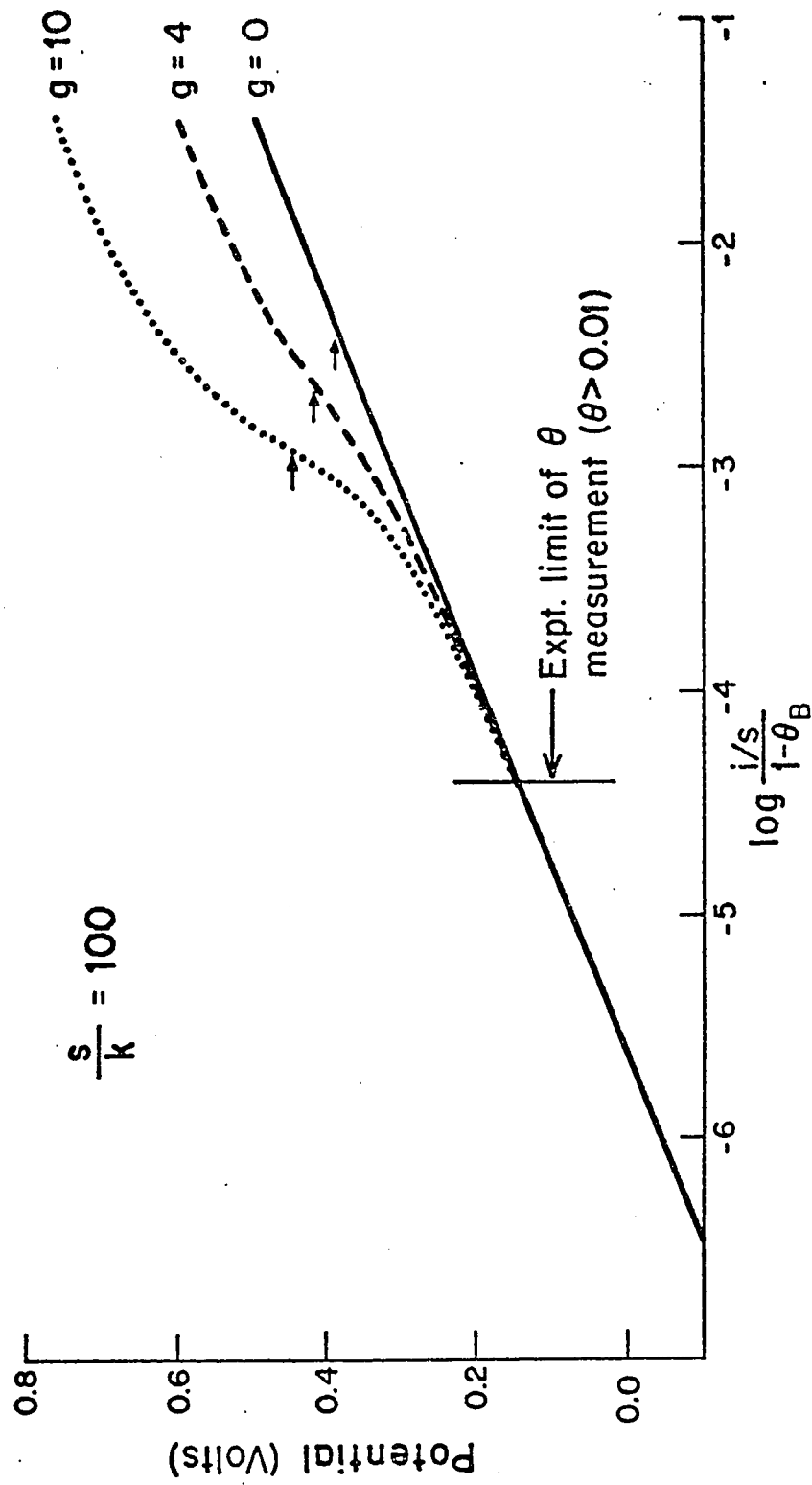


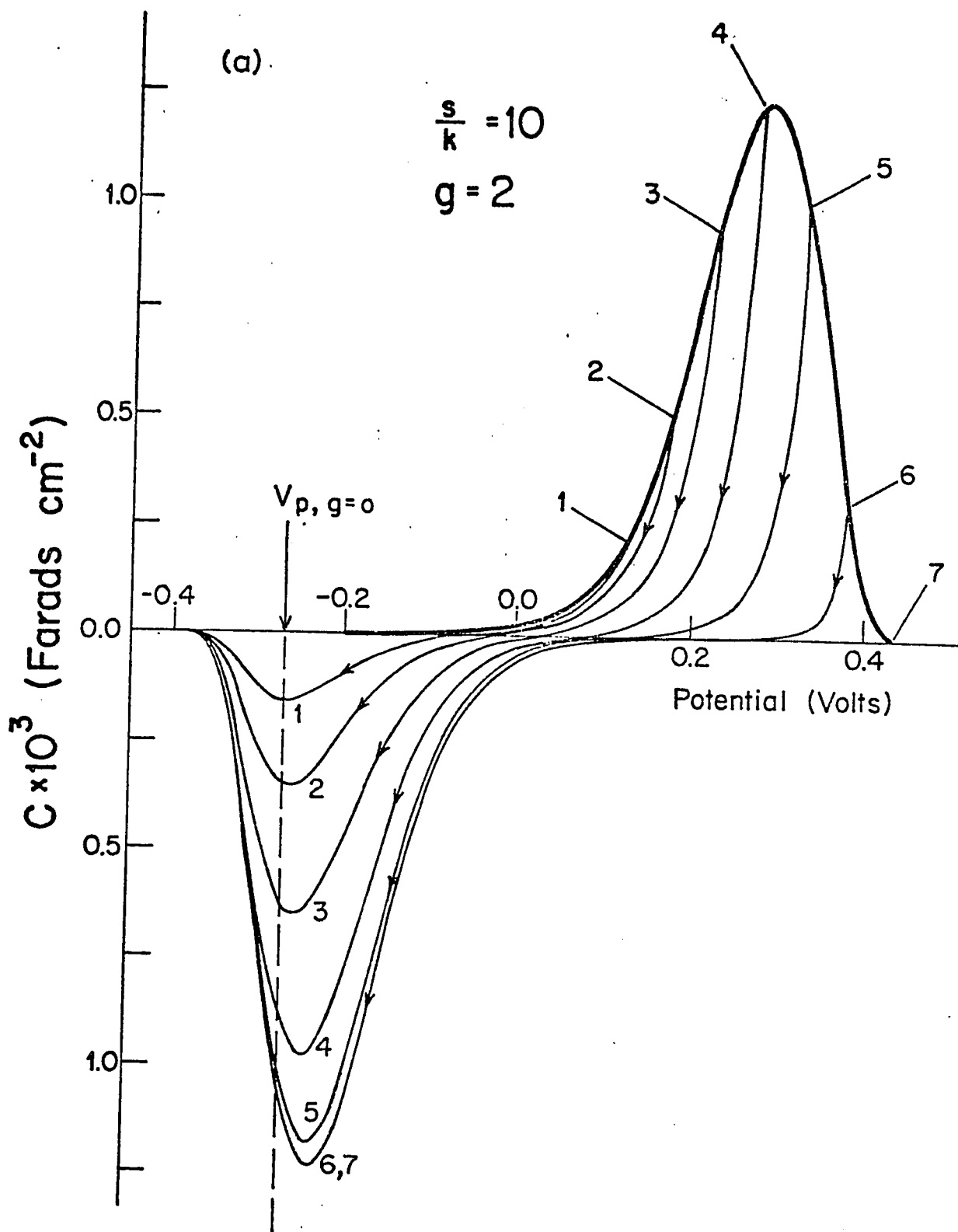
Fig. 4-10 Tafel type relations for reaction (1) under irreversible conditions ($\frac{s}{k} = 100$) for g values equal to 0, 4 and 10. Arrows show position of maxima in the corresponding C-V profiles.

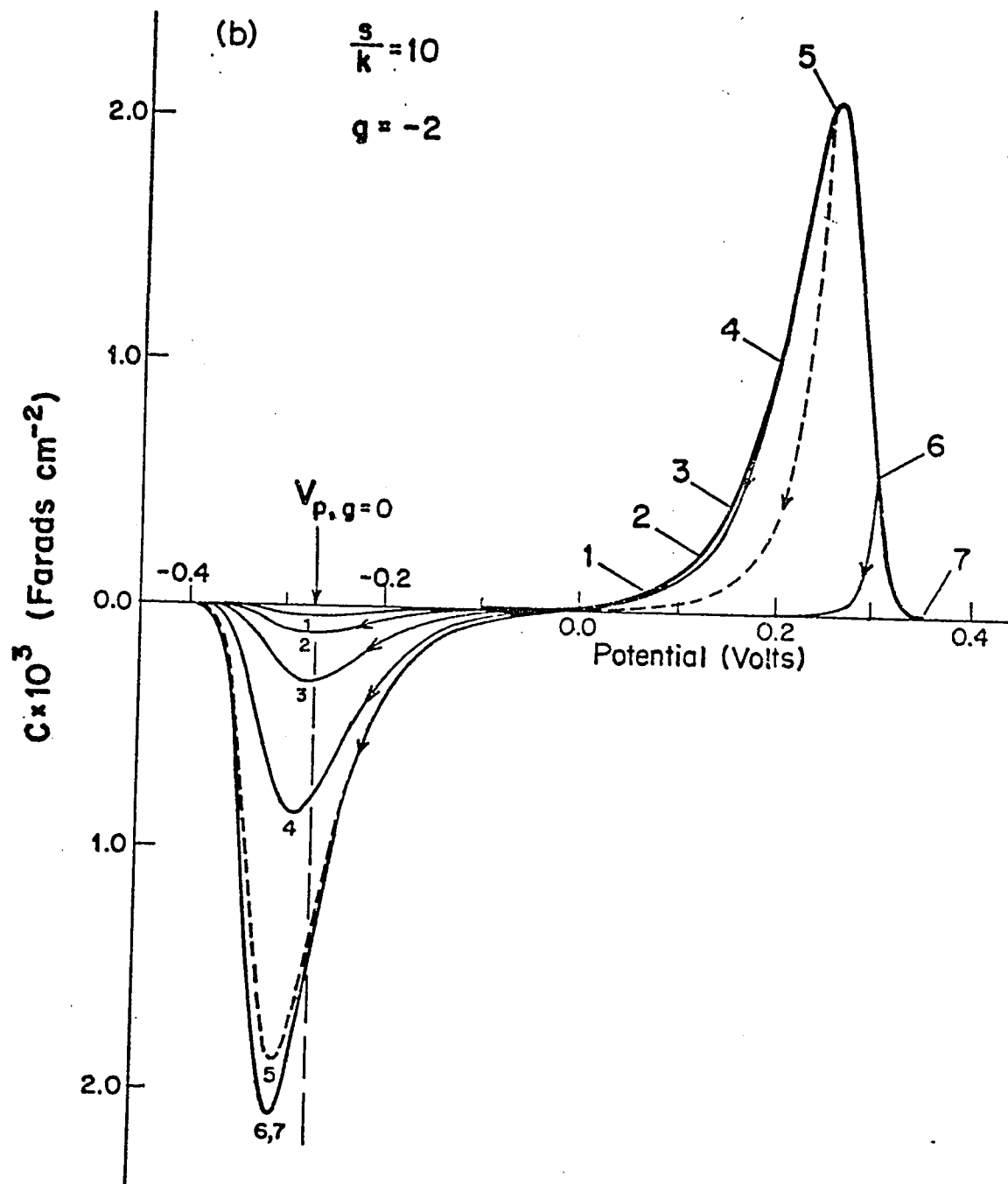
increasingly as $g > 0$. Below $\theta_B = 0.01$ a common Tafel-type line arises for all g values (except unrealistically high ones). This is as expected, since the low values of θ_B , multiplied by g , are then insufficient to cause significant deviations from "Langmuir" ($g = 0$) kinetics. For negative values of g the deviations from the Tafel line would be expected to occur in the opposite direction than for positive g values. The other explanations are similar to those discussed for $g > 0$.

4.6 Sweep Reversal During Formation of the Monolayer

A useful procedure in the study of chemisorbed species at electrodes which can indicate if $g \neq 0$ for the adsorbed layer is to successively reverse the sweep, in a multisweep experiment, at progressively more positive or negative potentials, i.e., at progressively increasing coverages. For reversible conditions (Fig. 4-3a), independently of the g factor involved, the reverse curve will always be a mirror image on the potential axis of the forward curve. For totally irreversible conditions, however, the reverse C vs. V profile is displaced from the forward profile but, if $g = 0$, the form of the C vs. V profile does not change with the quantity of adsorbed species involved; only the height of the curves increases as more B is desorbed in the reverse reaction of (I), (Fig. 4-3d). When $g > 0$, the free energy of the adsorbed layer increases (apart from its usual θ -dependent component $RT \ln \frac{\theta_B}{1-\theta_B}$) with coverage [eqn. (4-3)], so that the reverse sweep curves correspond to situations of more, or less, interaction in the surface film, i.e., the value of $g\theta_B$ corresponding to the initial θ_B in the reverse sweep is larger the greater the coverage. From eqn. (4-1), it

- Fig. 4-11 (a) Simulation of irreversible C-V profiles ($\frac{s}{k} = 10$), taking successive reverse sweeps from various potentials at which an incomplete monolayer has been formed in the previous forward sweep. g is taken as 2.
- (b) As in (a) but for $g = -2$.





is seen that this will enhance the back reaction current so that with increasing θ_B the back reaction current peak appears at more positive potentials. A similar, but opposite, explanation can be given for the case of $g < 0$.

Simulation of the sweep reversal operation is shown in Figs. 4-11a and 4-11b for an irreversible example of reaction (I) with $g = 2$ and -2 , respectively. The point of interest is that the current peaks on the reversed sweep for various increasing coverages generated in the forward sweep, corresponding to the curves marked 1 to 7 on Fig. 4-11a, thus appear at progressively more positive potentials when $g = 2$ (or generally $g > 0$) than the single-valued potential ($V_{p,g=0}$) for the case of $g = 0$ (cf. Fig. 4-3d). When $g = -2$ (Fig. 4-11b) (or for the general case $-4 \leq g < 0$) the peak potentials in the reversed sweep move to more negative potentials in the series of curves 1 to 7 as the initial coverage of B species being reduced increases.

Fig. 4-12 shows a more extreme case of Fig. 4-11a where g is taken as 10 and a series of ten sweep reversal curves are plotted.

4.7 Summary of the Characteristic Behaviour of a 1-e Electrochemical Surface Reaction

From the C-V profiles for reaction (I) under both reversible and irreversible conditions, a number of characteristic features of the kinetic behaviour, depending on the interaction parameter g , may be derived (see Figs. 4-1, 4-4 and 4-5). It is important to obtain a series of such profiles ranging from reversible to irreversible behaviour for reaction (I). The reversibility and irreversibility of

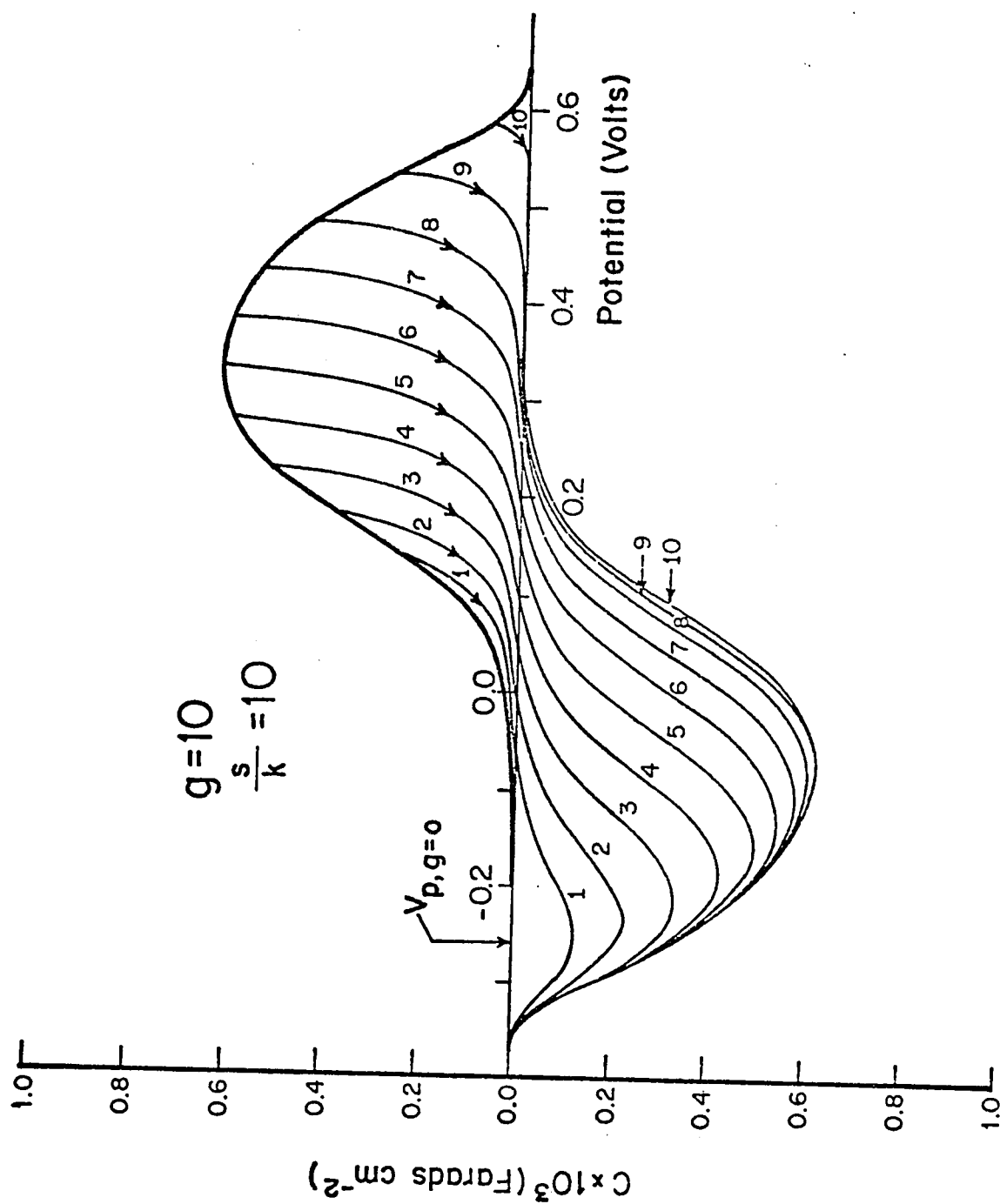


Fig. 4-12 Simulation of potential-sweep curves for reaction (I) for a more extreme case of $g=10$, with reversal of the sweeps at successively more positive potentials prior to that where a complete monolayer has been formed in the previous forward sweep.

the reaction is not determined by the applied sweep-rate, s , but rather by the reduced sweep-rate, s/k . The kinetic parameters, i.e., rate constants k_1' and k_{-1} and the other parameters such as the standard electrode potential E° and the value of g , can be determined from quantities such as C_p , V_p , $\theta_{B,p}$ and $\Delta V_{1/2}$ which depend on $\log \frac{s}{k}$ (see Figs. 4-2, 4-8 and 4-9).

A useful and important technique for study of the chemisorbed species B at the electrode surface is to reverse the sweep at the end of the anodic C-V profile and also prior to completion of the monolayer, i.e., before a complete anodic C vs. V profile is generated (see Figs. 4-3a-d, 4-11a,b and 4-12).

From the following, the interaction parameter g may be evaluated:

- (i) The values of $\Delta V_{1/2}$ corresponding to the reversible and irreversible behaviour of reaction (I);
- (ii) The values of $\theta_{B,p}$ when reaction (I) behaves irreversibly;
- (iii) The shift of the cathodic V_p and the change of the $\Delta V_{1/2}$ value of a cathodic i-V profile with the coverage established at the end of the previous anodic sweep under irreversible conditions in reaction (I).

CHAPTER V

THEORETICAL SIMULATION OF THE KINETIC RELAXATION METHOD

FOR DISTINCTION OF CO-ADSORBED SPECIES FROM TWO

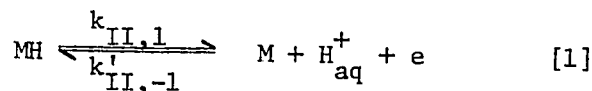
PARALLEL REACTIONS

5.1 Introduction

In certain electrocatalytic reactions, co-adsorption of more than one electroactive intermediate of the type discussed in Chapter IV may arise. The charge under the overall potentiodynamic current-potential profile for the adsorbed species may not then be used to evaluate coverage by each of the species. A method is proposed for resolution of processes involving more than one electrochemisorbed species when the electroactivity of, e.g., two species arises over a common potential range, and is based on the different kinetic relaxation response of "reversibly" electrosorbed species from that for more "irreversibly" electrosorbed species. In electrocatalytic reactions, especially those involving electro-oxidation or electrochemical hydrogenation, co-adsorption of organic intermediates with OH, O or H species often arises. Applications to the case of reduction of adsorbed nitriles at Pt⁶¹ enabled a two-stage mechanism to be formulated.

In this chapter, a new method which provides a basis for distinction between co-adsorbed electroactive species on an electrode in terms of the different rates of response of the two (or more)

species to a potential-pulse regime, i.e., in terms of the distinguishable kinetic relaxation characteristics which the surface electrochemical reactions exhibit, is described. Using this theoretical basis, simulations of the kinetic relaxation behaviour are made for a two-component process. Two anodic electrochemical surface reactions are considered, one fast and one slow. The former, for example, may involve chemisorbed H in a scheme such as:



where C represents an adsorbed electroactive molecule*, e.g., a nitrile⁶¹, capable of being reduced to adsorbed B (or further) in an electron transfer step and B can be reoxidized (cf. ref. 61) back to C on the surface as in reaction [2] above. Either the B or C molecules can be assumed to arise from a species in solution and chemisorb in a non-electrochemical step. Since this chemisorption step is considered to be very fast and irreversible, it is not taken into consideration in the calculations in the present chapter. It should be pointed out,

* It is important to mention at this point in the thesis that one should not confuse the letter C in this context with the same symbol used for pseudocapacitance. In the reaction [2] above, the letter C is merely used as the next letter in alphabetical order to represent the species originating in the electrochemical reaction, and in other reaction sequences in the later chapters, originating in either an electrochemical or chemical reaction step. It is felt that no confusion can arise between the two distinct meanings of the same letter thus used.

however, that reaction [2] involves displacement of a proton as well, since the chemisorbed species C are usually not charged (see also Chapter IV, Part 4.1, p.91).

5.2 Theoretical Description of the Kinetic Relaxation Method

The principles involved may be illustrated as follows. In an electrode process involving only the formation or reduction of an adsorbed species, no continuous Faradaic processes can occur. If, however, a linear potential sweep is applied, an electrode process will occur in response to this sweep and give a current-potential (i-V) profile which normally exhibits a maximum^{56,90}. If, during such a potential sweep, the sweep-rate s is suddenly increased for a short time from s_1 to s_2 , the current for a given species will immediately increase from an initial value i_1 to a new value i_2 at a given potential in the sweep, and the condition $\frac{i_1}{s_1} = \frac{i_2}{s_2}$ will hold if the surface electrochemical reaction is a fast reversible one for which

$$i = Cs \quad (5-1)$$

where C is the adsorption pseudocapacitance, as mentioned previously (see, e.g., Chapter I, p.27). If the electrode process is, however, not fast in relation to the time scale of the higher sweep-rate s_2 , the current i_2 will not be able to adjust to the new sweep-rate and the value i_2 will be lower than $i_1 \cdot (\frac{s_2}{s_1})$. A trailing current profile will then result for such a slow process (cf. Fig. 4-3).

When a fast reversible reaction component arises together with a slow one due to a second electroactive species co-adsorbed on

the electrode, it should therefore be possible to distinguish their current contributions in a linear potential sweep experiment by the response of the two processes to an instantaneously applied change of s from a low to a higher value (and vice versa). The equivalent circuit for this type of situation^{54,56}, involving two electroactive co-adsorbed species exhibiting different adsorption pseudocapacitances^{31,58,90} C_1 and C_2 and reaction rate constants (see reaction mechanism (II), p.109) may be represented as shown in Fig. 5-1. It should be pointed out that the solution resistance R_s is normally small and no overall continuous Faradaic reaction is considered.

C_1 and C_2 are the potential-dependent pseudocapacitances corresponding to potential-dependence of coverages of the two electroactive species. $1/R_1$ and $1/R_2$ correspond to potential-dependent electrochemical rate constants for the surface reactions involved and $C_{d.l.}$ is the double-layer capacitance. C_1 and C_2 have potential-dependent, non-zero values when the coverages θ of the species concerned are between 0 and 1 and they will be small for coverages approaching 0 or 1. A fast reversible component corresponds to a low value of the resistance R over the potential range of the sweep concerned (and vice versa).

5.3 Calculation Procedure and Values of Parameters

For details about the simulation technique employed, reference is made to Chapter III and Appendix I (see also Chapter IV, Part 4.2).

It is assumed that there are no diffusion limitations arising in reaction mechanism (II) in both reactions [1] and [2]. Double-layer

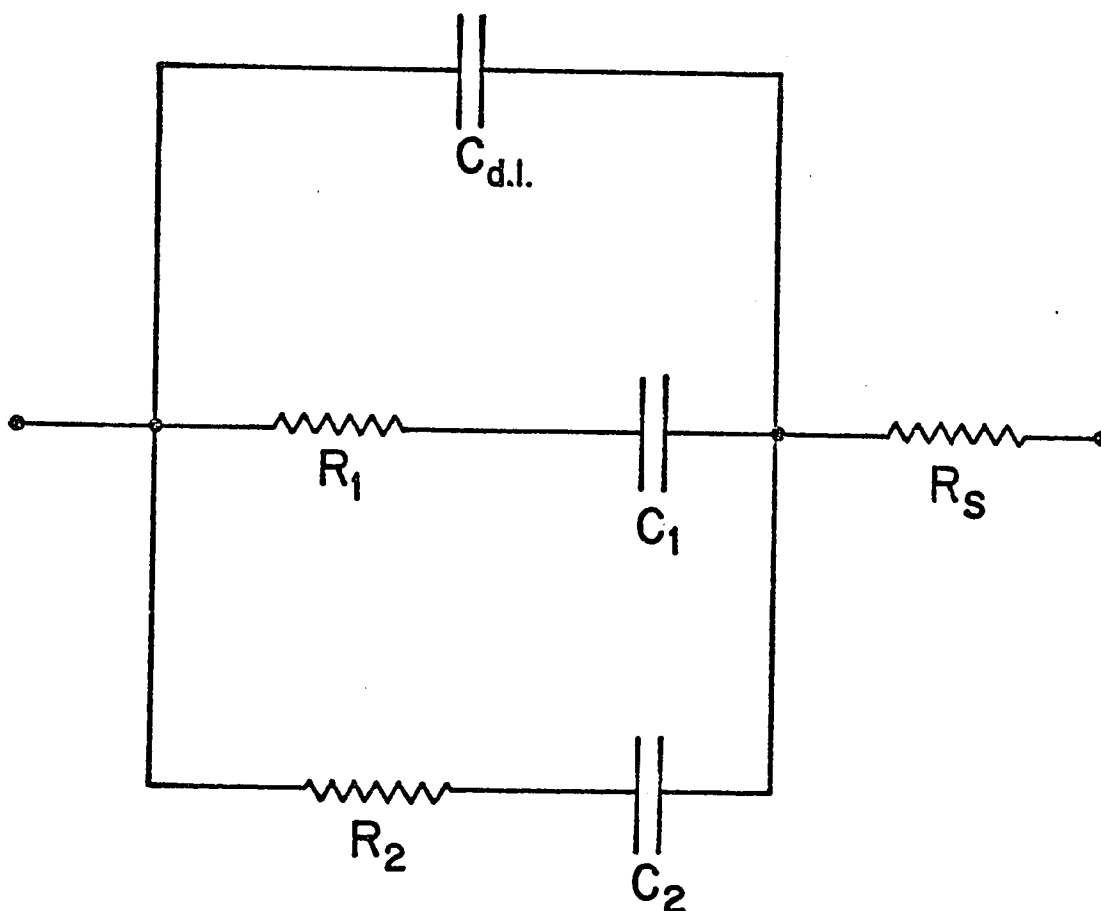


Fig. 5-1 Equivalent circuit representing two parallel electrochemical surface reactions. The two electroactive co-adsorbed species are assumed to exhibit different adsorption pseudocapacitances C_1 and C_2 . The potential-dependent electrochemical rate constants are inversely proportional to the resistances R_1 and R_2 . $C_{d.l.}$ is the double-layer capacitance and R_s the solution resistance.

factors are considered to be constant and are not included in the equations to be derived in Part 5.3, except implicitly in the rate constant values, k .

In the present calculations, the charge for generating overall monolayer coverage of the three adsorbed species H, B and C in reaction (II) was taken as $Q = 220 \mu\text{C cm}^{-2}$ as for H on Pt, to simplify the calculations. In reality, the charge for oxidation of a monolayer of B need not be the same as that for oxidation of a monolayer of H adsorbed on Pt. For example, for a 2-e reduction (or oxidation) in the case of adsorbed nitriles on Pt surface⁶¹ the charge for a monolayer is $277 \mu\text{C cm}^{-2}$. Again, for convenience, the hydrogen ion concentration, c_{H^+} , was taken as 1 mol l^{-1} (cf. Chapter IV, Part 4.2).

The values of other parameters, which are kept constant throughout the calculations, are the same as mentioned in Part 4.2 of the previous chapter.

5.4 Formulation of Kinetic Equations

The kinetic equations for reactions [1] and [2] of the reaction mechanism (II) under linear potential-sweep control may be written as follows:

$$-\frac{d\theta_{\text{H}}}{dt} = k_{\text{II},1} \theta_{\text{H}} \exp\left(\frac{\Delta V_1}{b}\right) - k'_{\text{II},-1} c_{\text{H}^+} (1 - \theta_{\text{H}} - \theta_{\text{B}} - \theta_{\text{C}}) \exp\left(-\frac{\Delta V_1}{b}\right) \quad (5-2)$$

$$-\frac{d\theta_{\text{B}}}{dt} = \frac{d\theta_{\text{C}}}{dt} = k_{\text{II},2} \theta_{\text{B}} \exp\left(\frac{\Delta V_2}{b}\right) - k_{\text{II},-2} \theta_{\text{C}} \exp\left(-\frac{\Delta V_2}{b}\right) \quad (5-3)$$

where $k_{II,1}$, $k'_{II,-1}$, $k_{II,2}$ and $k_{II,-2}$ are the rate constants. The forward and backward rate constants for a given reaction were taken to be equal, i.e., $k_{II,1} = k'_{II,-1}$ and $k_{II,2} = k_{II,-2}$. Since the value of $c_{H^+} = 1 \text{ mol l}^{-1}$, it is possible to write*

$$k_{II,-1} = k'_{II,-1} c_{H^+} \quad (5-4)$$

in order to simplify the explanations and descriptions of the graphs obtained in later parts of this chapter.

The modulating potential, ΔV , is given by (cf. Chapter IV, Part 4.3, p.93)

$$\Delta V = V - E^\circ = V_{in} \pm st - E^\circ \quad (5-5)$$

where ΔV_1 corresponds to the modulating potential referred to the standard electrode potential E_1° for the surface process [1] and ΔV_2 to E_2° . The two values of E° (E_1° and E_2°) may or may not be equal.

The total current density as a function of potential V in the sweep is the sum of i_1 , the current density for reaction [1], and i_2 , the current density for reaction [2], i.e.,

$$i_{Tot} = i_1 + i_2 \quad (5-6)$$

The individual currents are:

$$i_1 = Q \left(- \frac{d\theta_H}{dt} \right) \quad (5-7)$$

and

* For a more detailed explanation, refer to the footnote on p.96.

$$i_2 = Q(-\frac{d\theta_B}{dt}) = Q \frac{d\theta_C}{dt} \quad (5-8)$$

Interactions between the same or different adsorbed species are not considered here, neither are heterogeneity effects. This means that g is taken as zero. Finite values of g could be taken but the calculations are then more complex. For the purpose of illustrating the kinetic effects with two adsorbed species, the above conditions suffice.

In the calculations it was assumed that the total coverage $\theta_B + \theta_C$ due to species B and C is 66.7% and the maximum coverage for adsorbed H can reach only 33.3%. Both species block surface sites which would otherwise be available for H chemisorption.

5.5 Shapes of Current-Potential Curves in the Kinetic Relaxation Method

Solution of eqn. (5-2), when it is assumed that no species B and C are adsorbed on the surface, gives rise to the familiar i - V profiles shown in Figs. 5-2a,b. These profiles can be directly compared with the reversible C-V profiles for a simple 1-e electrochemical reaction, with g taken as zero. The H charge in Figs. 5-2a,b is taken as 33.3% of $220 \mu\text{C cm}^{-2}$ for the reasons explained in Part 5.4. The effect of changing the sweep-rate s during potential scanning is demonstrated in these two figures (i.e., Figs. 5-2a,b). The sweep-rate s was changed from 0.005 to 0.01 or 0.1 V sec^{-1} , for two different values of k_1^* for the case of hydrogen desorption from the surface of

* For better clarity when writing the rate constants, the abbreviations in this and other chapters indicating the reaction mechanism in question are omitted. Thus, $k_{II,1} = k_1$, $k_{II,-1} = k_{-1}$, etc. When the necessity arises for distinction between two or more reaction mechanisms, the subscripts will be retained.

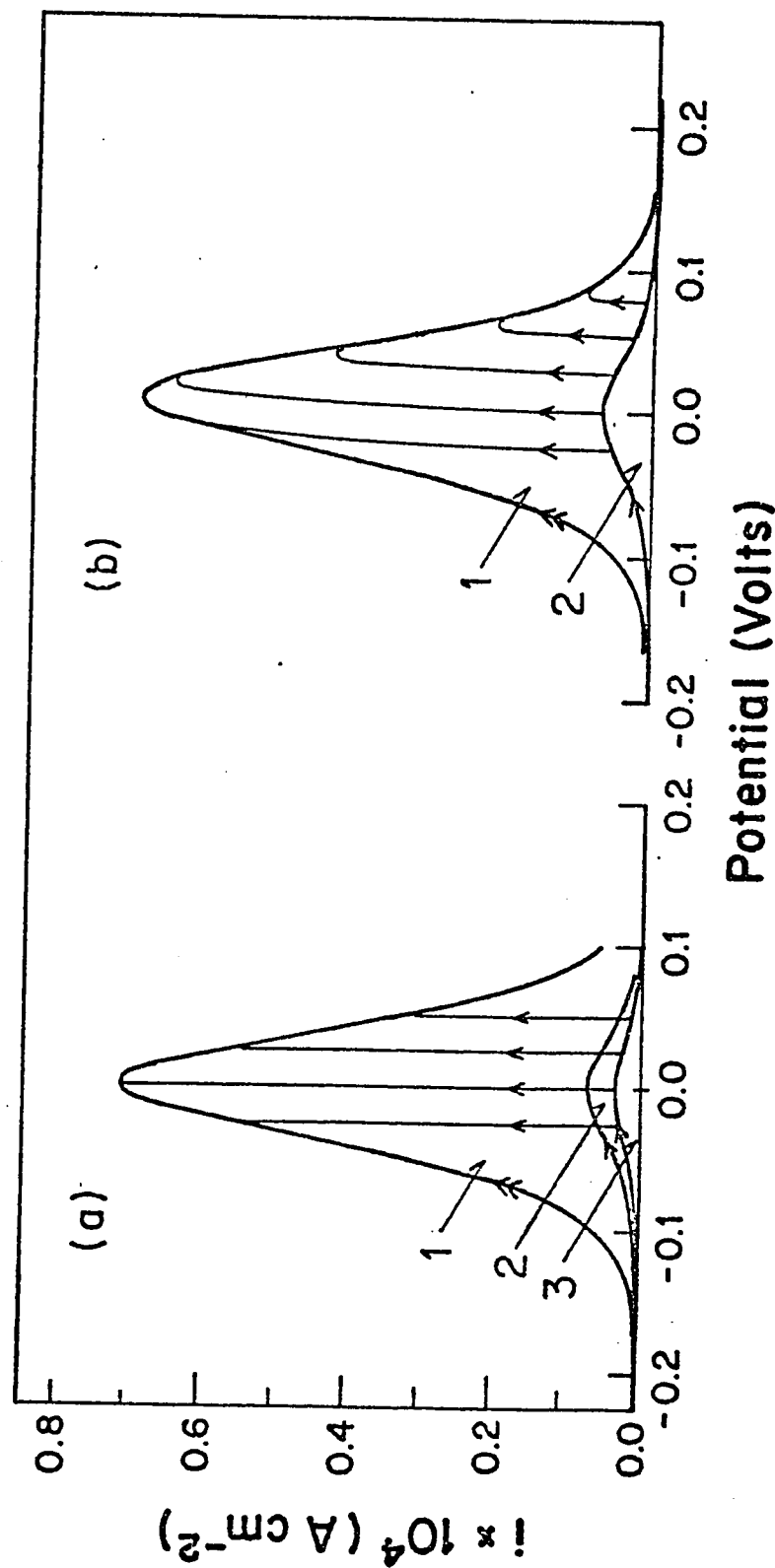


Fig. 5-2 Calculated i - V profiles for potentiodynamic sweeps with change of sweep-rate at various potentials when process [2] is not considered.

(a) $k_1 = k_{-1} = 100 \text{ sec}^{-1}$

1. $s = 0.1 \text{ V sec}^{-1}$

2. $s = 0.01 \text{ V sec}^{-1}$

3. $s = 0.005 \text{ V sec}^{-1}$

(b) $k_1 = k_{-1} = 10 \text{ sec}^{-1}$

1. $s = 0.1 \text{ V sec}^{-1}$

2. $s = 0.01 \text{ V sec}^{-1}$

(Roman capital pre-subscript numbers, indicating the reaction mechanism in question, have been omitted on the k terms for clarity in this and other diagrams both on the figures and in the captions to the figures).

the electrode. Change of s results in a rapid readjustment of current to a new, almost reversible potentiodynamic (i - V) profile but the extent of readjustment depends on s/k_1 value as is seen (Figs. 5-2a,b) for the case of $k_1 = 10 \text{ sec}^{-1}$ in comparison with $k_1 = 100 \text{ sec}^{-1}$. The former case gives some slowness in the final stages of approach to the higher overall i - V profile for a complete (uninterrupted) sweep. As the reduced sweep-rate s/k_1 is less than 0.01 V (see Chapter IV, Part 4.4) at all times, reversible or almost reversible i - V profiles will always result for these chosen conditions.

The combination of current components for desorption of H and oxidation of species B is shown in Figs. 5-3, 5-4, 5-5 and 5-6 for maximum $\theta_B = 66.7\%$ and $\theta_H = 33.3\%$. E° values are again taken arbitrarily as 0.0 V in Figs. 5-3, 5-4 and 5-5. Fig. 5-6 shows the current-potential behaviour for the case where E_2° value for reaction [2] is 0.05 V more negative than that for H (reaction [1]). For $s = 0.005 \text{ V sec}^{-1}$, change of s by a factor of 20 results in readjustment of the current (see Fig. 5-3) as in the H case alone (cf. Figs. 5-2a,b). As the potential is swept beyond the value where the sweep-rate was increased, an inflection in the i - V response is generated which depends on the values of s/k_1 and s/k_2 . Here it is process [2] which responds more slowly ($\frac{s}{k_2} > \frac{s}{k_1}$) to potential change than does the more reversible H process (reaction [1]) so that significant polarization is required to pass currents for process [2] that are comparable with those for the H process [1] at a given sweep-rate. Figs. 5-3 and 5-4 show that the system behaves in the same way when the ratios of the rate constants

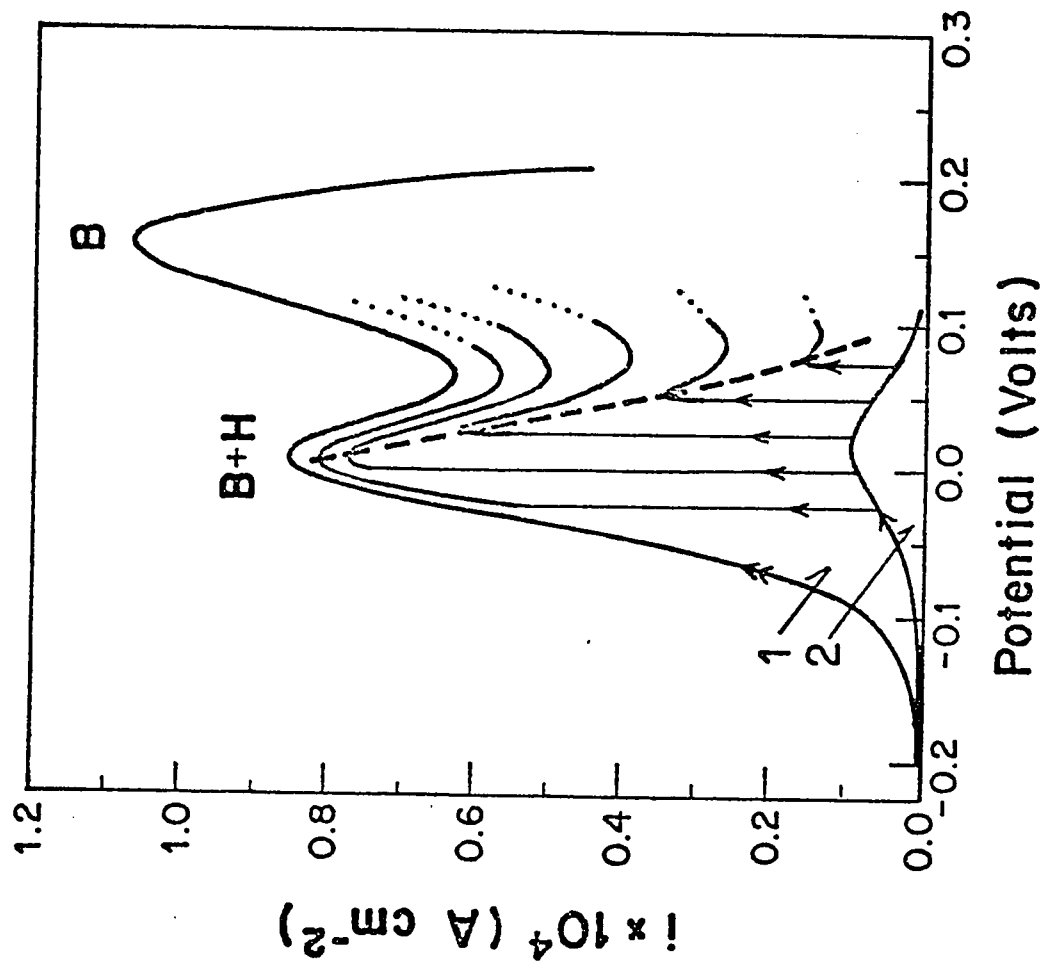


Fig. 5-3 Calculated i - V profiles for reaction mechanism (II) when the change of sweep-rate is initiated at various potentials. $E_1^0 = E_2^0 = 0.0$ V, $k_1 = k_{-1} = 100 \text{ sec}^{-1}$, $k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$

1. $s = 0.1 \text{ V sec}^{-1}$
2. $s = 0.005 \text{ V sec}^{-1}$

(Comparison is to be made with Figs. 5-4 and 5-5).

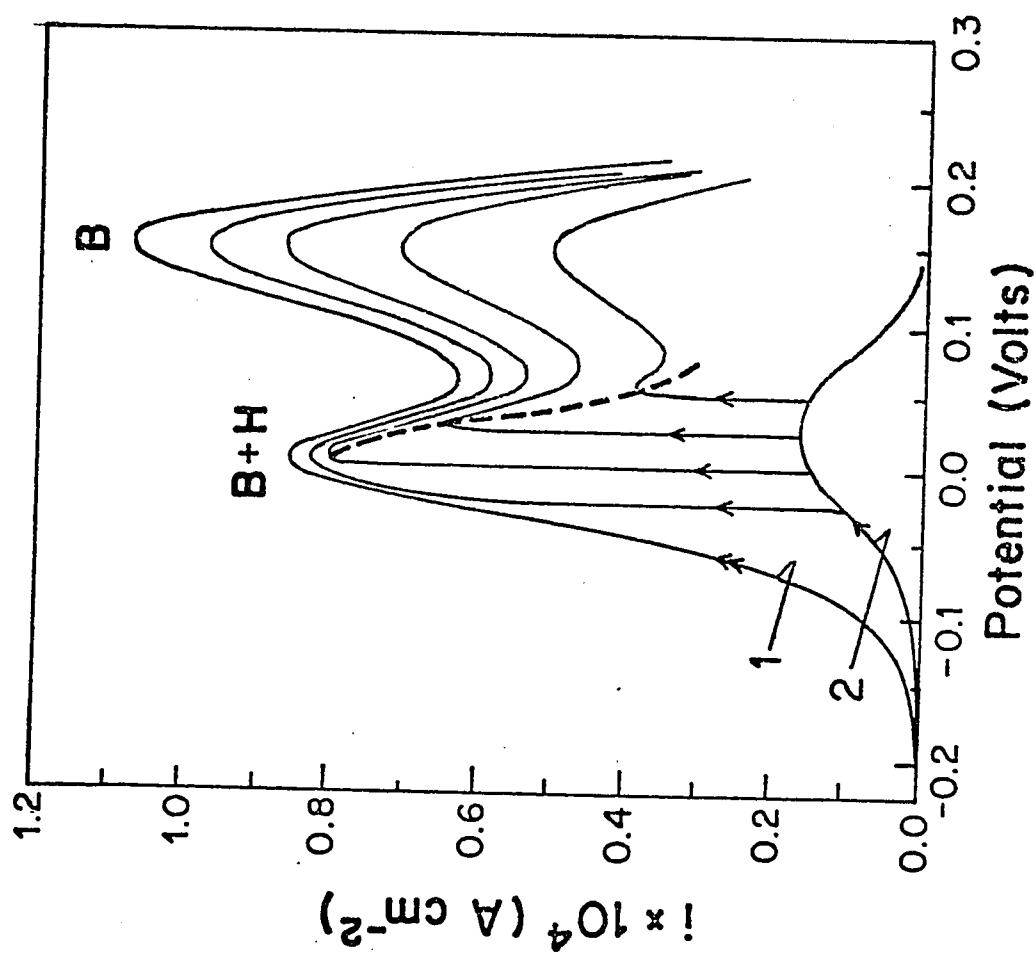


Fig. 5-4 Calculated i - V profiles for reaction sequence (II) when the change of sweep-rate is initiated at various potentials. $E_1^0 = E_2^0 = 0.0$ V,
 $k_1 = k_{-1} = 100 \text{ sec}^{-1}$, $k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$
 1. $s = 0.1 \text{ V sec}^{-1}$
 2. $s = 0.01 \text{ V sec}^{-1}$

(Comparison is to be made with Figs. 5-3 and 5-5).

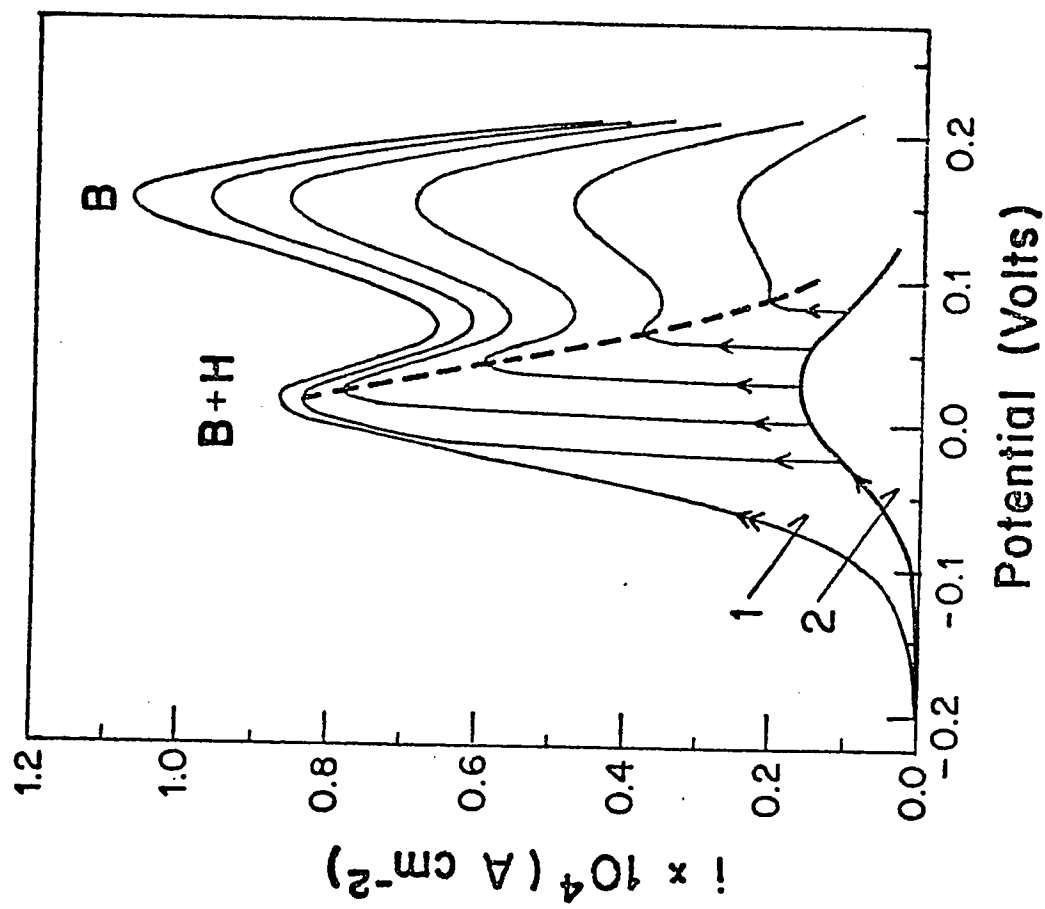


Fig. 5-5 Calculated i - V profiles for reaction mechanism (II) when the change of sweep-rate is initiated at various potentials. $E_1^0 = E_2^0 = 0.0$ V, $k_1 = k_{-1} = 10 \text{ sec}^{-1}$, $k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$
 1. $s = 0.1 \text{ V sec}^{-1}$
 2. $s = 0.01 \text{ V sec}^{-1}$

(Comparison is to be made with Figs. 5-3 and 5-4).

k_1/k_2 for the reaction [1] compared with the reaction [2], in relation to the values of s , are the same. Very little slowness in the final stages of current readjustment for the fast reaction is seen in Fig. 5-4. The only difference between the parameters of the two figures is the different value of s for the smaller sweep. In Fig. 5-3 the sweep is twice as slow as in Fig. 5-4. Fig. 5-5 shows how the system behaves when the ratio of the rate constants k_1/k_2 differs from that of Figs. 5-3 and 5-4. In this Fig. 5-5, the slowness even in the H case is already quite pronounced although the process [1] itself is still relatively reversible (cf. Fig. 5-2b).

In Fig. 5-6, where E_2° for process [2] is -0.05 V in comparison to $E_1^\circ = 0.0$ V for reaction [1], more overlap between the two peaks (B and B+H) arises, but the resolution of the fast H profile is again seen as the locus of limits of current response of the fast process to the change of sweep-rate s (dashed line).

Figs. 5-3, 5-4, 5-5 and 5-6 are to be compared with Figs. 5-2a,b for the H process alone. The B+H peaks in the four former figures are of course higher than that for H alone due to the overlap of the currents for the two processes on the potential scale, particularly between 0.0 and 0.1 V.

The computed i -V profiles provide a good basis for understanding the significance of the experimental behaviour of co-adsorbed species as shown in Figs. 5-7, 5-8 and 5-9a,b*. The locus in inflection points distinguishing the kinetics of the reversible from the less

* These figures were taken from ref. 61 with the permission of the authors.

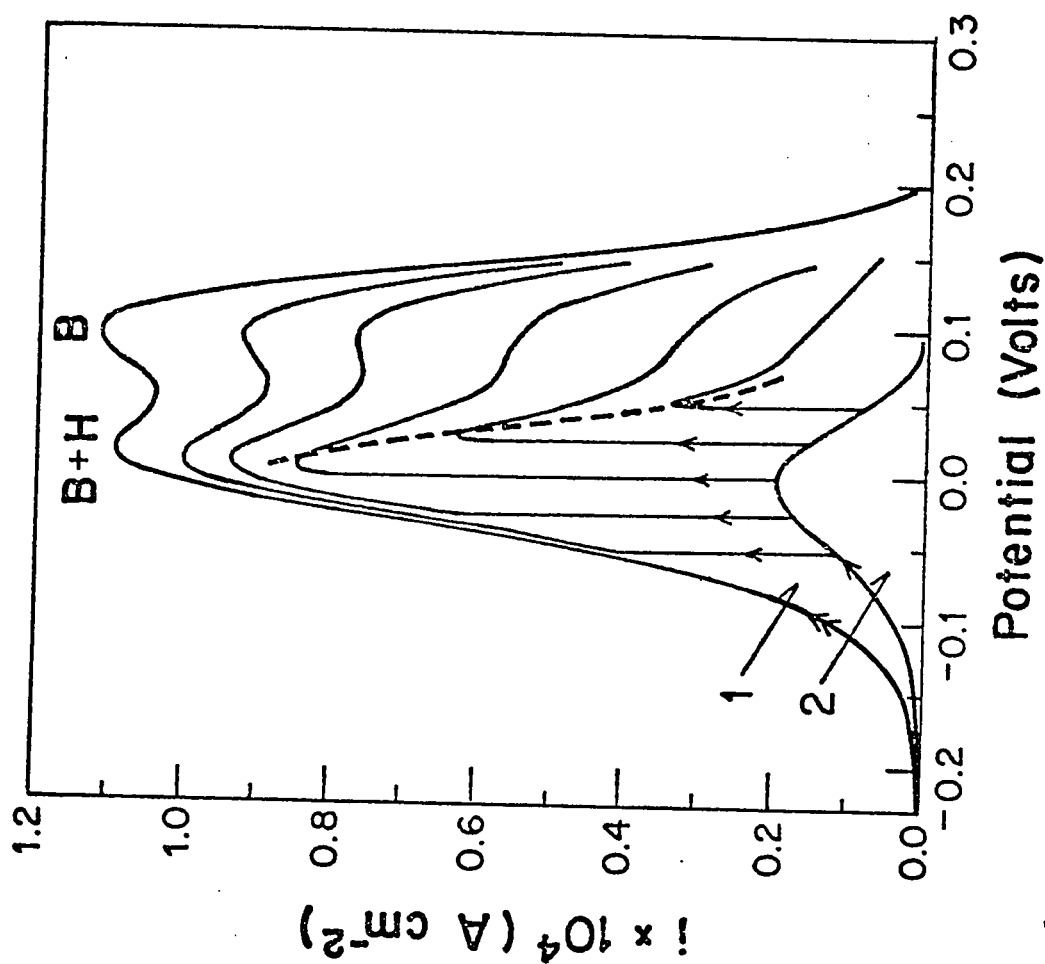


Fig. 5-6 Calculated i - V profiles for reaction sequence (II) when the change of sweep-rate is initiated at various potentials. $E_1^0 = 0.0$ V, $E_2^0 = -0.05$ V, $k_1 = k_{-1} = 100 \text{ sec}^{-1}$, $k_2 = k_{-2} = 0.1 \text{ sec}^{-1}$

1. $s = 0.01 \text{ V sec}^{-1}$
2. $s = 0.1 \text{ V sec}^{-1}$

(Comparison is to be made with Figs. 5-3, 5-4 and 5-5).

reversible process evidently provides a satisfactory basis for distinction of co-adsorbed electroactive species (see Part 5.6 below for more detailed discussion of the experimental results) and enables their individual coverages to be evaluated.

5.6 Application of the Kinetic Relaxation Technique to Experimental Systems

The following discussion of the experimental results of electrosorption of acetonitrile which chemisorbs at platinum electrodes, uses the results obtained and conclusions reached by Angerstein-Kozłowska et al.⁶¹ to exemplify the use of the kinetic relaxation technique in a real system*.

Since the adsorbed CH_3CN species, which can be chemisorbed on Pt without reaction at high anodic potential (~ 0.75 V), is itself electroactive in the adsorbed state in the hydrogen and double-layer regions (i.e., between about 0.0 to 0.7 V with respect to an hydrogen reference electrode), the observed current-potential profile in the H-region cannot be assumed to be due only to deposition or ionization of H itself. It is therefore important in this case, and also more generally, to be able to distinguish co-adsorbed H from other adsorbed organic species that may be reactive in the H-region. Resolution of the H deposition or ionization, and the acetonitrile reduction or reoxidation processes, may be made by the kinetic relaxation method described in Part 5.2 and this case provides a good example of its application and potential. It should be pointed out that in the

*This aspect of the present work is published in ref. 74.

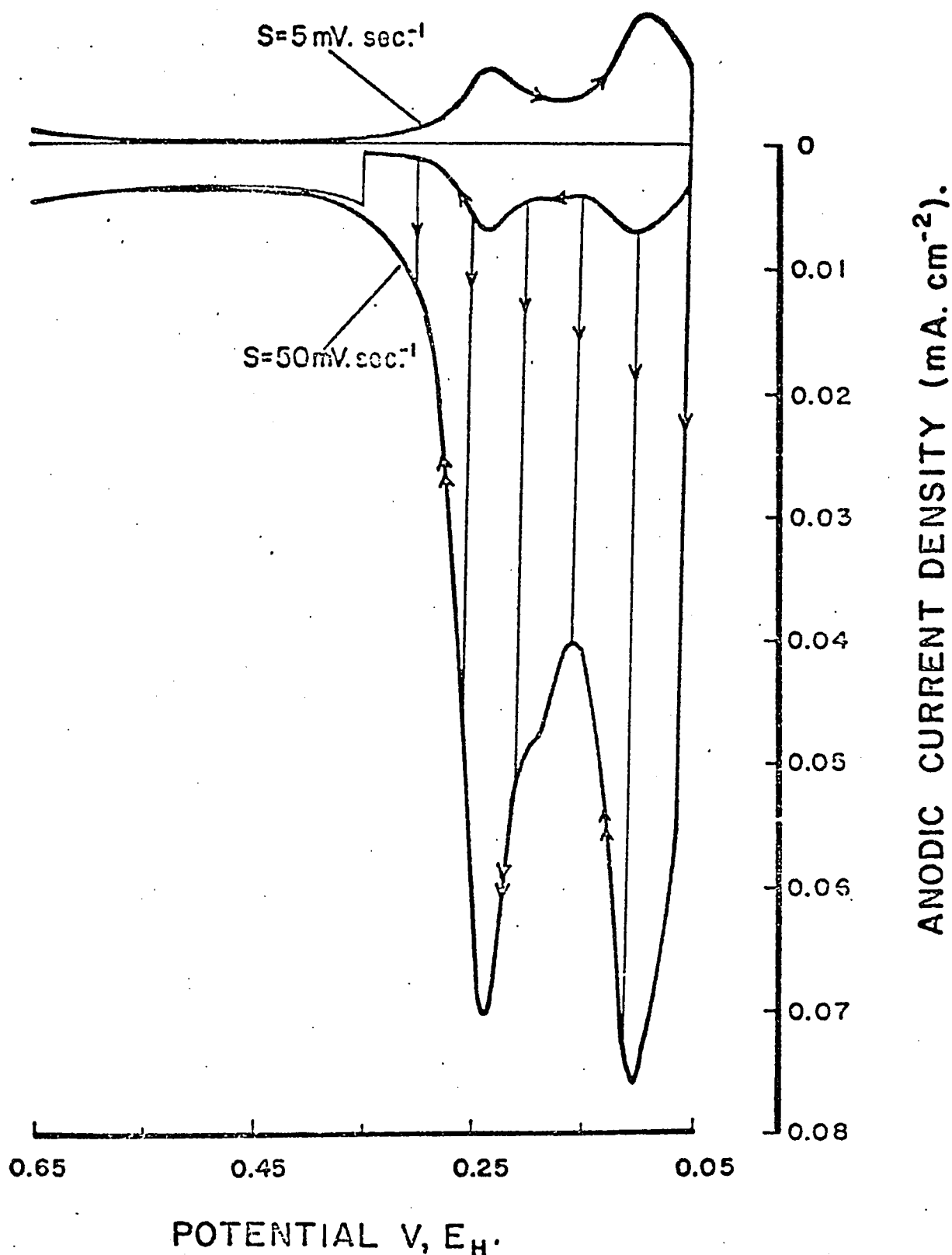


Fig. 5-7 Fast response of reversible H desorption process (anodic-going sweep) at Pt in 1N aqueous H_2SO_4 to a sudden change of sweep-rate from slow (5 mV sec^{-1}) to fast (50 mV sec^{-1}) one. Continuous i-V curves show the profiles for repetitive sweep conditions at the two sweep-rates. (From Ph.D. thesis of B. MacDougall, Ottawa, 1973).

H-potential region direct adsorption of CH_3CN from solution occurs by anodic H-displacement⁶¹.

The typical fast response of a reversible process to a sudden change in sweep-rate is shown in Fig. 5-7 for hydrogen ionization at Pt in the absence of acetonitrile. Change of sweep-rate from $s_1 = 5 \text{ mV sec}^{-1}$ to $s_2 = 50 \text{ mV sec}^{-1}$ at various potentials in the anodic-going sweep causes an immediate increase of current to a common i-V profile, corresponding to the profile obtained for an applied continuous higher sweep-rate $s_2 = 50 \text{ mV sec}^{-1}$ (cf. Figs. 5-2a,b simulated by computer).

The current-potential profile in the presence of acetonitrile⁶¹ is exemplified in Fig. 5-8. It can be seen that part of the reduction occurs over the double-layer potential region and is completed in the H-potential region. It must be stressed that this process is a slower one and the maximum extent of reduction is only achieved⁶¹ by holding the potential at the end of the cathodic sweep.

Separation of reaction components in the H region can be achieved by means of the following potentiodynamic sweep programme. A slow (e.g., 5 mV sec^{-1}) cathodic or anodic-going sweep in the H-region was established and then much faster (e.g., $50\text{--}500 \text{ mV sec}^{-1}$) cathodic or anodic sweeps were initiated successively from various potentials in this region from the slower "guiding" sweep (5 mV sec^{-1}).

Application of the above procedure enables the profiles of Fig. 5-8 to be resolved into slow and fast reaction component profiles in both the H deposition (cathodic sweep) and ionization (anodic sweep)

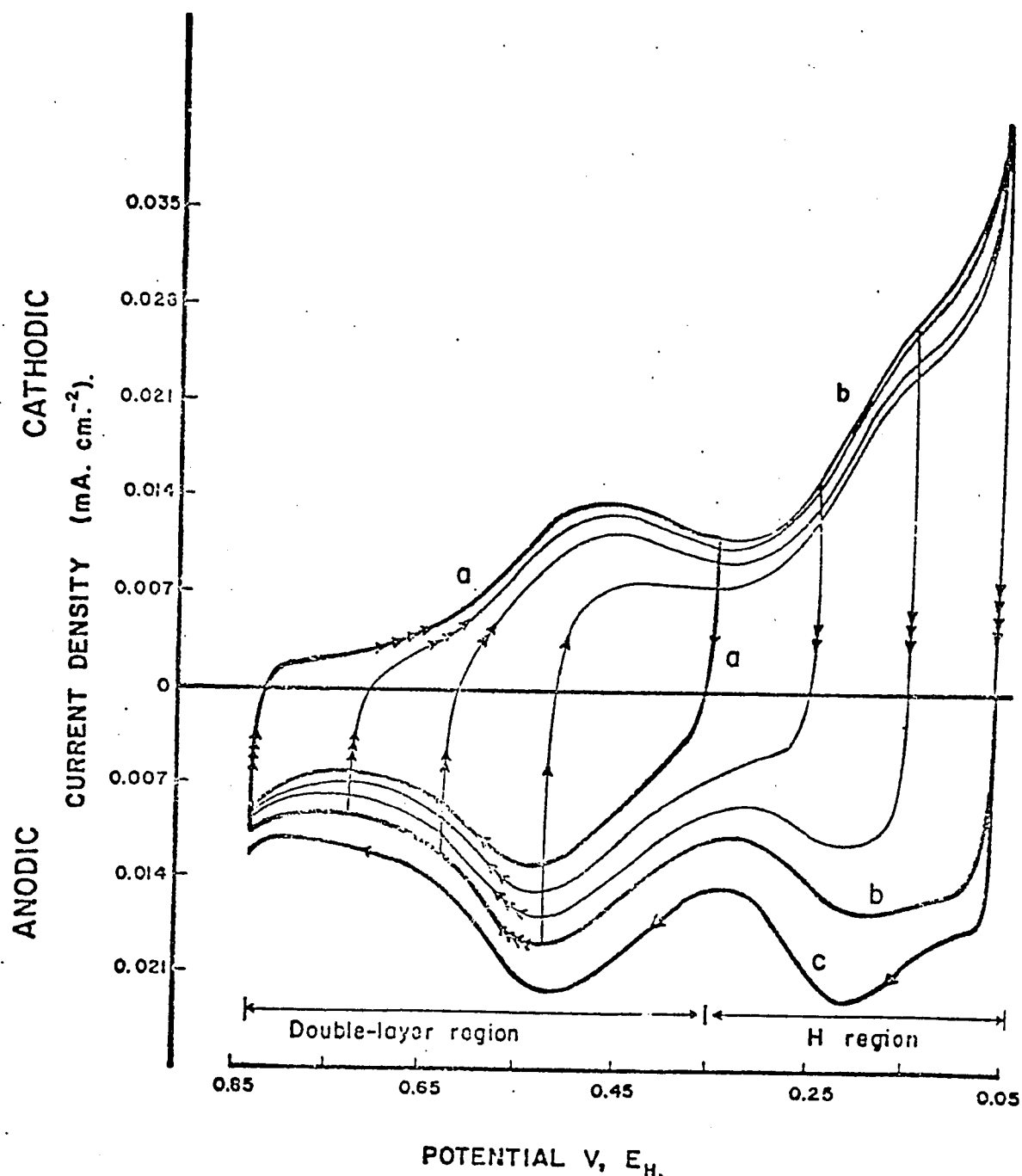


Fig. 5-8 Anodic and cathodic peaks in potentiodynamic i - V profiles for adsorbed acetonitrile over various potential ranges obtained by reversing the direction of the sweep at different potentials in both the anodic-going and cathodic-going sweep; curve (a) for the double-layer region; curve (b) for double-layer and H regions, curve (c) with holding of potential at 0.06 V, E_H for 90 sec. $[\text{CH}_3\text{CN}] = 5 \times 10^{-3} \text{ M}$; $s = 50 \text{ mV sec}^{-1}$.
(From Ph.D. thesis of B. MacDougall, Ottawa, 1973).

regions. Fig. 5-9a shows the behaviour obtained when the sweep-rate is increased 100 times from 5 mV sec^{-1} while Fig. 5-9b exemplifies the response when the increase is only 10 times from the same slow "guiding" sweep. The extent of hydrogen co-adsorption is calculated from the integral under the limits of fast current response and the exact charge on both the cathodic and anodic-going sweeps confirms this fact. The amount of adsorbed CH_3CN species in both the oxidation or reduction regions is determined by difference from the overall cyclic voltammetry i - V profile (see Figs. 5-9a,b). From the experimental results obtained, it was shown that about 68% of the surface Pt sites are blocked by chemisorbed CH_3CN while 32% remain available for H chemisorption⁶¹.

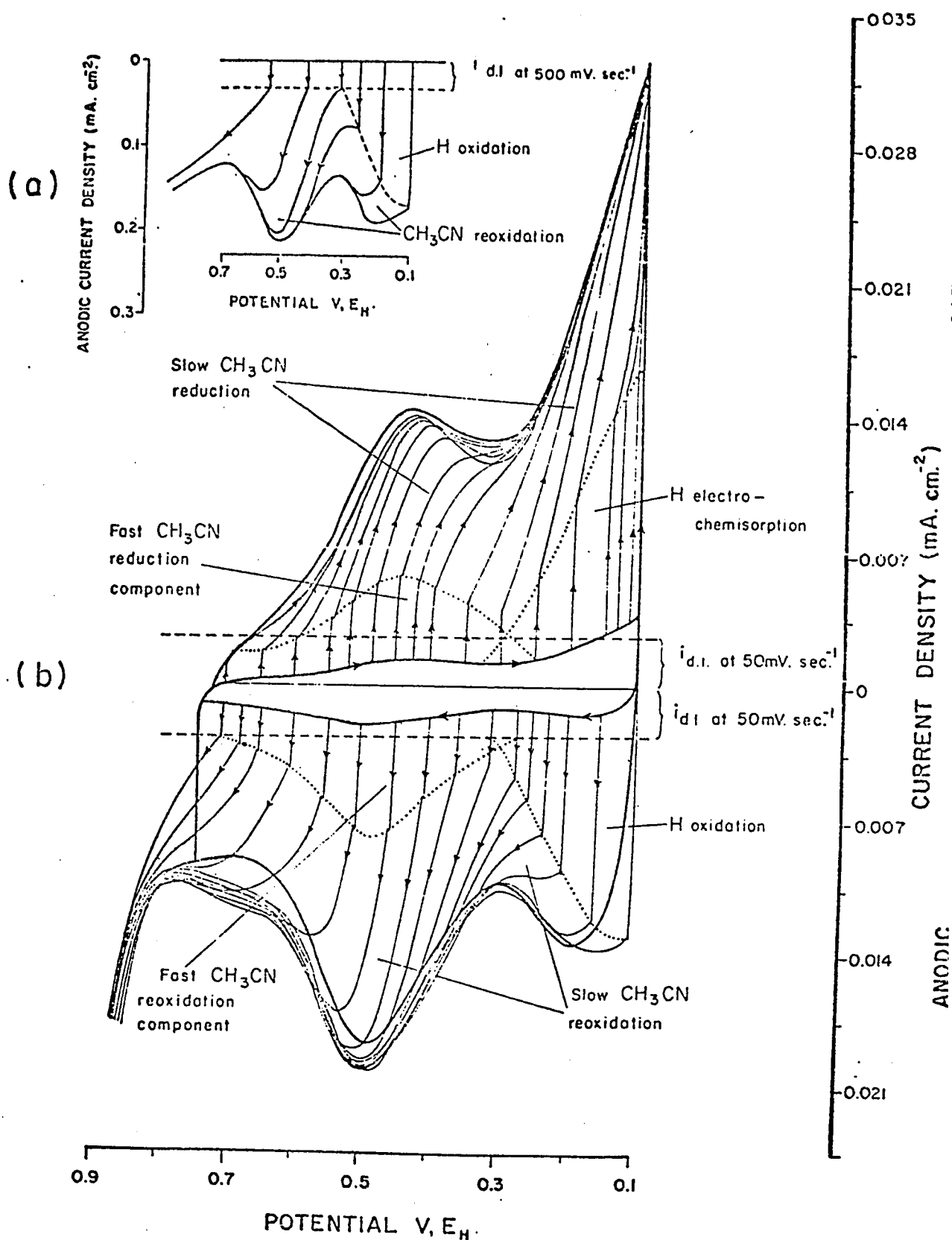


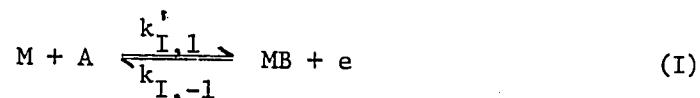
Fig. 5-9 (a) Resolution of fast H ionization and acetonitrile processes with transients at 500 mV sec⁻¹ taken on a slower anodic sweep of 5 mV sec⁻¹
 (b) Resolution of the fast atomic hydrogen and acetonitrile processes obtained by initiating faster transients (50 mV sec⁻¹) on a slower anodic or cathodic-going one (5 mV sec⁻¹).
 (From Ph.D. thesis by B. MacDougall, Ottawa, 1973).

CHAPTER VI

COMPUTER SIMULATION OF THE KINETIC BEHAVIOUR OF SEQUENTIAL SURFACE REACTIONS INVOLVING ADSORBED SPECIES

6.1 Introduction

The general behaviour of a first-order, 1-e surface reaction

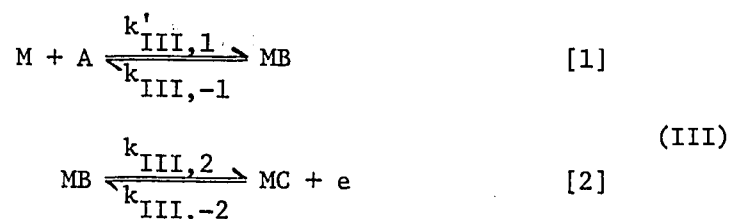


under linear potential sweep conditions was described in Chapter IV and the characteristic features were emphasized. In this chapter it will be shown that other, diagnostically useful, characteristic features may be developed when the 1-e surface reaction is coupled with a first-order chemical step. Further treatments of more complex cases will be given in subsequent chapters.

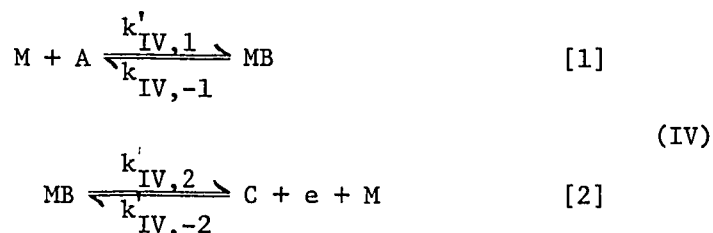
Applicability of a given model mechanism to an experimental situation can often be inferred from the qualitative features of the kinetic behaviour; then, for a given mechanism, determination of other factors such as relative values of rate constants, the value of α^* and values of equilibrium constants can be derived. The methods involved will be described for three sequential two-step reactions. The relevant literature on previous electrochemical studies of sequential reactions involving chemisorbed species was quoted in Chapter I, Section 1.5.2.2.

* Here α is the transfer coefficient defined by $\frac{1}{\alpha} = \frac{F}{RT} \frac{dV}{d \ln i}$.

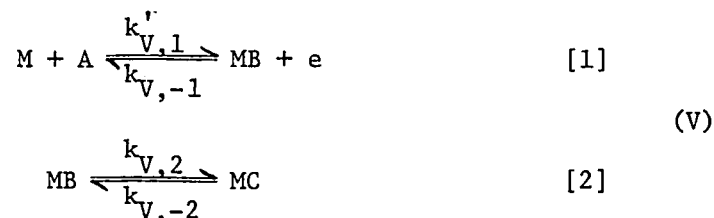
The model case of a simple first-order process in which a species A in solution becomes adsorbed on to free metal sites M producing a chemisorbed species B which then undergoes electrochemical oxidation to another species C^{*}, or vice versa, was investigated. Three cases of interest arise: (i) a reaction sequence (III), when species C remains chemisorbed on the surface:



(ii) a sequence (IV), when C is formed from adsorbed B as a solution-soluble species, thus regenerating free surface sites:



(iii) a reaction sequence (V), when the formation of the species B occurs in an electrochemical step, as in reaction (I), but is followed by a first-order chemical step on the surface to form adsorbed species C:



* See footnote p.109 for detailed explanation.

The reaction schemes (III) and (IV) represent "ce" types of mechanisms, while (V) is an example of an "ec" mechanism.

The kinetic behaviour under linear potential-sweep control of "ec" and "ce" type surface reactions involving chemisorbed species was evaluated theoretically by computer simulation calculations. Characteristic features, which arise in comparison with those of the simple 1-e reaction involving deposition of a chemisorbed species, will be emphasized. Especially the value of the $\Delta V_{1/2}$ parameter for various conditions and the effect of holding the potential at the end of a sweep on the subsequent reverse sweep behaviour are of interest.

6.2 Calculation Procedure and Values of Parameters

In the present series of computations for the cases of sequential reactions, the same calculation methods were used as in previous chapters (Chapters IV and V). Also, all the calculations were made, if not otherwise stated, for the same conditions as in Chapters IV and V, viz. $k_1 = k_{-1}$ and $k_2 = k_{-2}$ in the three sequences. The standard electrode potential E° for the electrochemical step was taken as zero, the charge Q to form a monolayer of adsorbed species as $220 \mu\text{C cm}^{-2}$ and the symmetry factor β as 0.5. No diffusion limitation was considered. The concentration c_A of A in solution in all three cases as well as the concentration c_C of C in solution in reaction mechanism (IV) are taken as 1 mol l^{-1} .

In the calculations, it has been assumed that both species B and C, when chemisorbed on M, follow Langmuir isotherms. Criteria

can, however, be developed for detection of significant interaction effects ($g \geq 0$).

The equations used for computer calculations have been formulated for the forward sweep going in the "anodic" direction and the backward sweep in the "cathodic" direction. A change in which the forward sweep is taken as "cathodic" or the backward one "anodic", is trivial.

6.3 Features of the C-V Profiles that are to be Sought for Characterizing the Mechanism and Kinetic Behaviour of the Reaction Sequences

It is necessary to calculate a series of C-V profiles for the various reaction sequences for a range of sweep-rates, $s = \frac{dV}{dt}$, which cover values of s sufficiently small that both the chemical and electrochemical reaction steps are maintained almost in equilibrium during the sweep, to values of s sufficiently large that both reaction steps are driven to a state of complete irreversibility. (In an experimental analysis, a similar range of s would be employed.) Then the following characteristic features of the electrochemical kinetic behaviour can be considered:

- (i) the overall shape of the C-V profile which gives the first indication of the participation of a chemical reaction coupled with the charge-transfer process;
- (ii) the dependence on sweep-rate, s , of the pseudocapacitance C , the peak potential V_p , the half-width of the peak, $\Delta V_{1/2}$, and the coverage to the peak, θ_p ;

- (iii) the presence and type of time effects occurring during holding the potential constant at the beginning or end of a sweep, as indicated by the C-V behaviour in a following reverse sweep.

6.4 Reaction Sequence (III)

6.4.1 Formulation of kinetic equations

The following equations were used for computation of the current density, i , as a function of potential, V , in the sweep at a sweep-rate s :

$$\frac{d\theta_B}{dt} = k'_{III,1} c_A (1 - \theta_B - \theta_C) - k_{III,-1} \theta_B - k_{III,2} \theta_B \exp\left(\frac{\Delta V}{b}\right) + k_{III,-2} \theta_C \exp\left(-\frac{\Delta V}{b}\right) \quad (6-1)$$

and

$$\frac{d\theta_C}{dt} = k_{III,2} \theta_B \exp\left(\frac{\Delta V}{b}\right) - k_{III,-2} \theta_C \exp\left(-\frac{\Delta V}{b}\right) \quad (6-2)$$

the current being taken as

$$i = Q \frac{d\theta_C}{dt} \quad (6-3)$$

where θ_B and θ_C are the surface coverages of species B and C, respectively, and c_A is the concentration of species A in solution in mol l^{-1} . $k'_{III,1}$, $k_{III,-1}$, $k_{III,2}$ and $k_{III,-2}$ are the forward and backward rate constants of the two processes above. The modulating potential, ΔV , is given by [cf. eqn. (4-2)]

$$\Delta V = V_{in} \pm st - E_2^\circ \quad (6-4)$$

where E_2° is the standard electrode potential for the electrochemical surface reaction, which is related to the standard electrode potential for the overall reaction by

$$E^\circ = E_2^\circ + \frac{RT}{F} \ln \frac{k'_{III,1}}{k_{III,-1}} \quad (6-5)$$

and other terms have been defined previously. At time $t=0$, θ_B was assumed to be the equilibrium coverage determined by the isotherm for formation of adsorbed species B and θ_C was taken as 0.

6.4.2 General form of families of C vs. V profiles

The features, which can distinguish sequence (III) from a simple 1-e electrochemical reaction (I), can be seen from Figs. 6-1 and 6-2. In these figures the characteristic changes of the C-V profiles from reversible to irreversible conditions as the reduced sweep-rate [$s/k_{I,1}$ for reaction (I) and $s/k_{III,2}$ for reaction sequence (III)] increases are shown for reaction (I) (Fig. 6-1, cf. Fig. 4-1 and ref. 90) in comparison with the profiles for three different k_1/k_2 ratios for reaction sequence (III) (Figs. 6-2a,b,c). The values of $k_1 = k_{-1}$ were chosen so that the chemical step [1] became progressively more irreversible in relation to the electrochemical step [2].

For reaction (I), as was described in Chapter IV, the peak pseudocapacitance C_p diminishes with increasing s from its value for the reversible case ($C_{p,rev.}$) to a new constant value ($C_{p,irrev.}$) for the completely irreversible process, the ratio $C_{p,rev.}/C_{p,irrev.}$ being

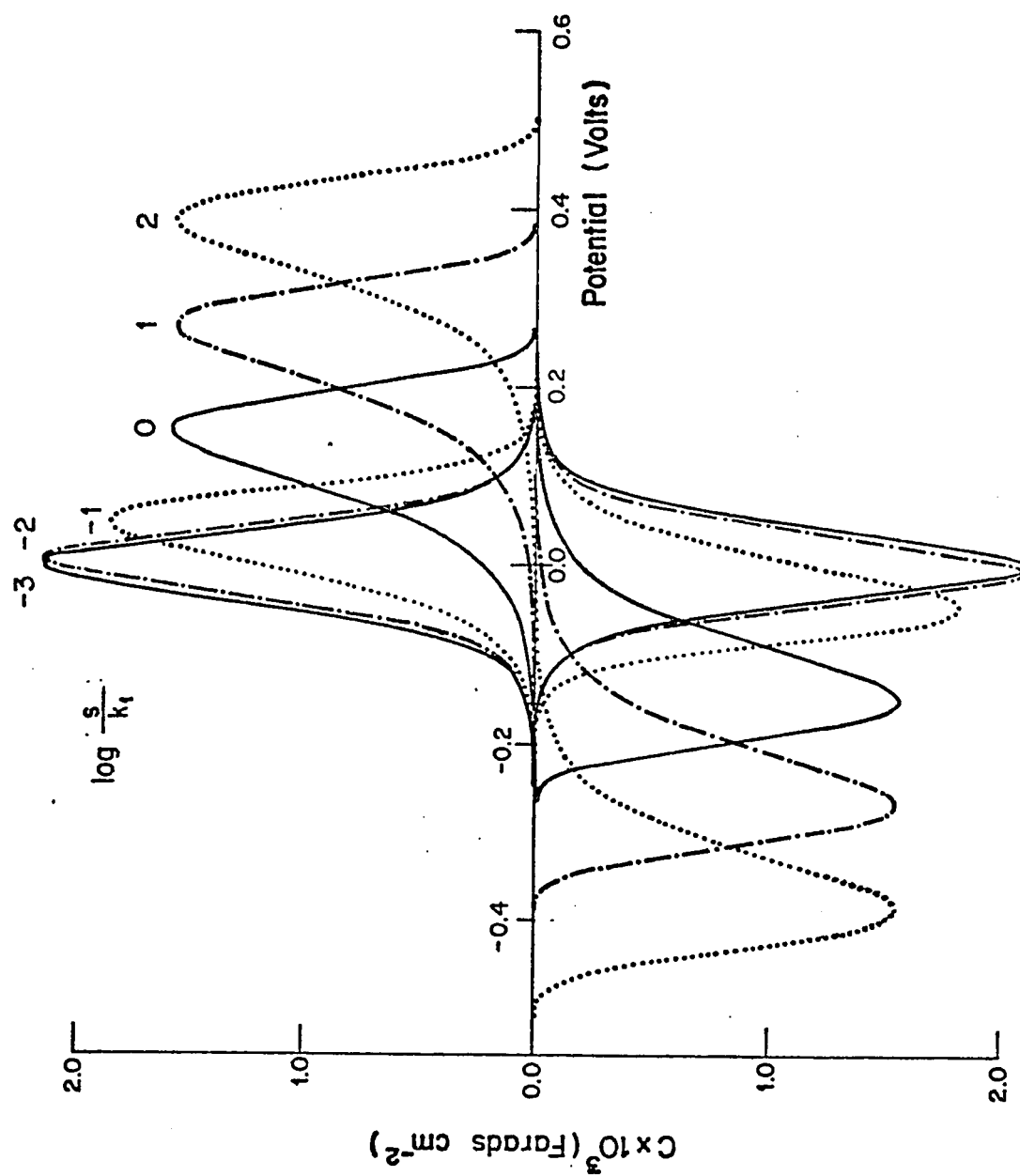


Fig. 6-1 Anodic and cathodic C-V profiles for the 1-e surface reaction (I) for various s/k_1 values showing progression from reversible to irreversible behaviour (cf. Chapter IV and ref. 90).

1.36 for $g=0$. The change in C_p occurs over about 2 decades of s . As is well known^{90,92}, the peaks for the reversible and irreversible cases have characteristic shapes (see also Chapter IV).

For reaction sequence (III), the general shape of the C-V profiles is different and depends strongly on the ratio of rate constants, k_1/k_2 . It is found that the following features, characteristic of this type of reaction sequence, can be distinguished (Figs. 6-2a,b,c):

- (i) the anodic C-V profile differs from the cathodic one;
- (ii) the ratio $C_{p,rev.}/C_{p,irrev.}$ for the anodic profile is always larger than for the reaction (I) and depends on the initial value of coverage, θ_{in} , of species B. The transition of the peak of pseudocapacitance from reversible to irreversible behaviour can occur over more than 5 decades of sweep-rate (Fig. 6-2a), or peaks with different shapes and heights can appear in the potential range of the reversible peak (Fig. 6-2c);
- (iii) a broad peak appears with current tailing off as the potential increases. For higher s , the tail on the peak profile becomes longer, eventually being transformed into a limiting current (see Fig. 6-2a, curve for $\log \frac{s}{k_2} = 2$, 6-2b for $\log \frac{s}{k_2} = 0$, and 6-2c for $\log \frac{s}{k_2} = -2$);
- (iv) it can be inferred that if the rate of the chemical step [1] is comparable with that of the electrochemical step [2] then cyclic voltammetry will change the

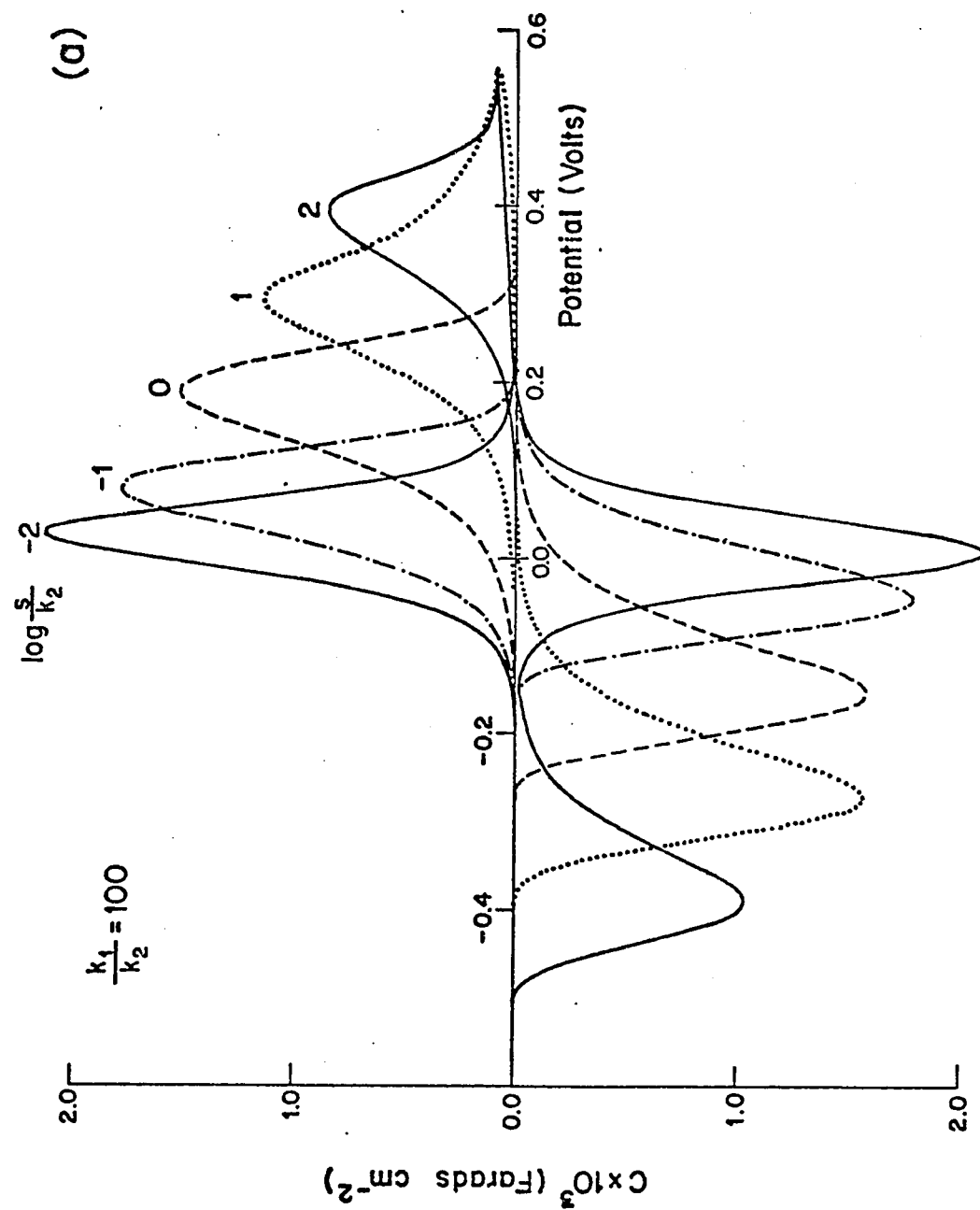
Fig. 6-2 Anodic and cathodic C vs. V profiles for reaction sequence (III) for various s/k_2 values showing change from reversible to irreversible behaviour of step [2] for various k_1/k_2 ratios:

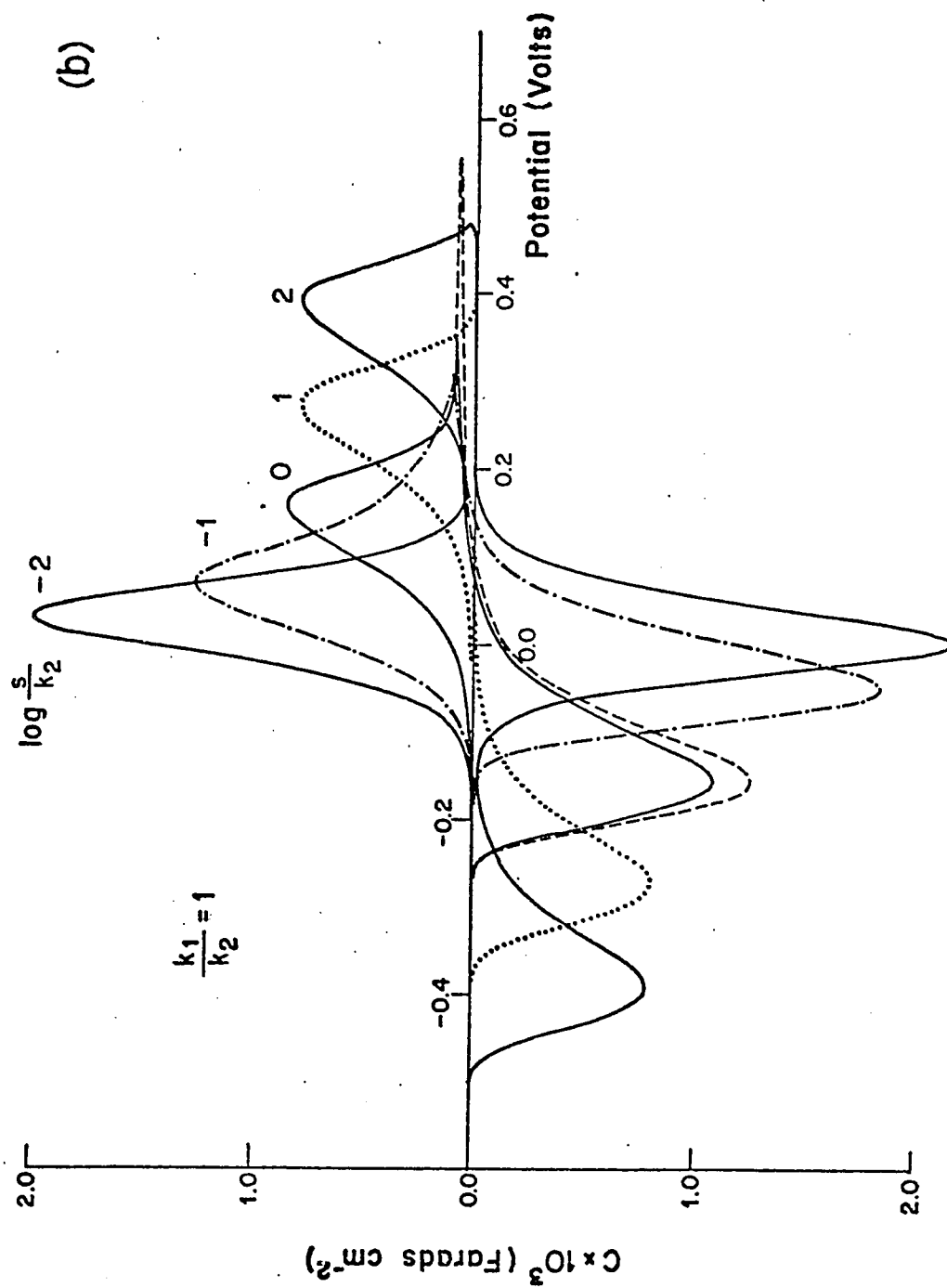
(a) $\frac{k_1}{k_2} = 10^2$

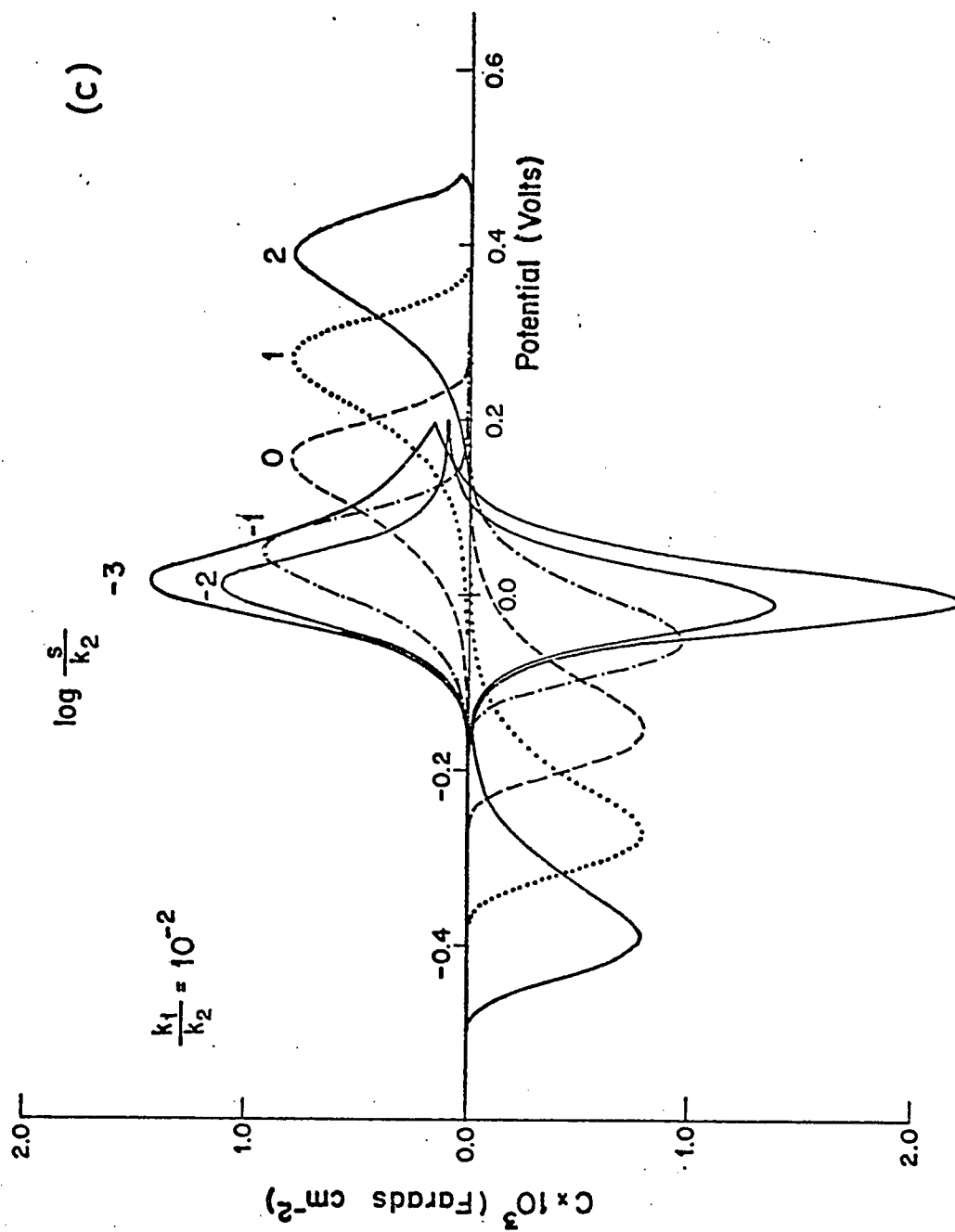
(b) $\frac{k_1}{k_2} = 1$

(c) $\frac{k_1}{k_2} = 10^{-2}$

Comparison is to be made with Fig. 6-1.







successive anodic and cathodic C-V profiles until a condition arises where the same quantity of species B formed during the anodic-going sweep is removed in the cathodic-going sweep for a given set of anodic and cathodic potential limits. It is only then, that the C-V profile will remain unchanged in further multisweeps.

In Fig. 6-3 is shown a series of plots of peak C values (C_p) for reaction (III) as a function of $\log \frac{s}{k_2}$ derived from plots such as Figs. 6-2a,b and c. Analogous plots for $\Delta V_{1/2}$ and θ_p , the coverage to the peak potential, are shown in Figs. 6-4 and 6-5. Depending on the ratio of the rate constants for the chemical (k_1) and the electrochemical (k_2) steps, C_p can assume various values (Fig. 6-3). Two limiting cases can be distinguished:

- (a) when coverage of species B is maintained at its equilibrium value (Fig. 6-5) under all conditions, i.e., when reaction [1] is reversible on the time-scale of the sweep, $C_{p,rev.}$ or $C_{p,irrev.}$ will have the same values as for reaction (I) leading to a fully covered layer ($\theta_C = 1$);
- (b) if step [1] is irreversible on the time-scale of the sweep, $C_{p,rev.}$ or $C_{p,irrev.}$, $\theta_{B,p}$ and $\theta_{C,p}$ for reversible or irreversible conditions will have lower values, proportional to whatever initial value of θ_B is established at the beginning of the sweep. This can be seen in Fig. 6-6 for $C_{p,irrev.}$ corresponding to various initial θ_B values equal to 0.8, 0.5 and 0.2. However, the shape

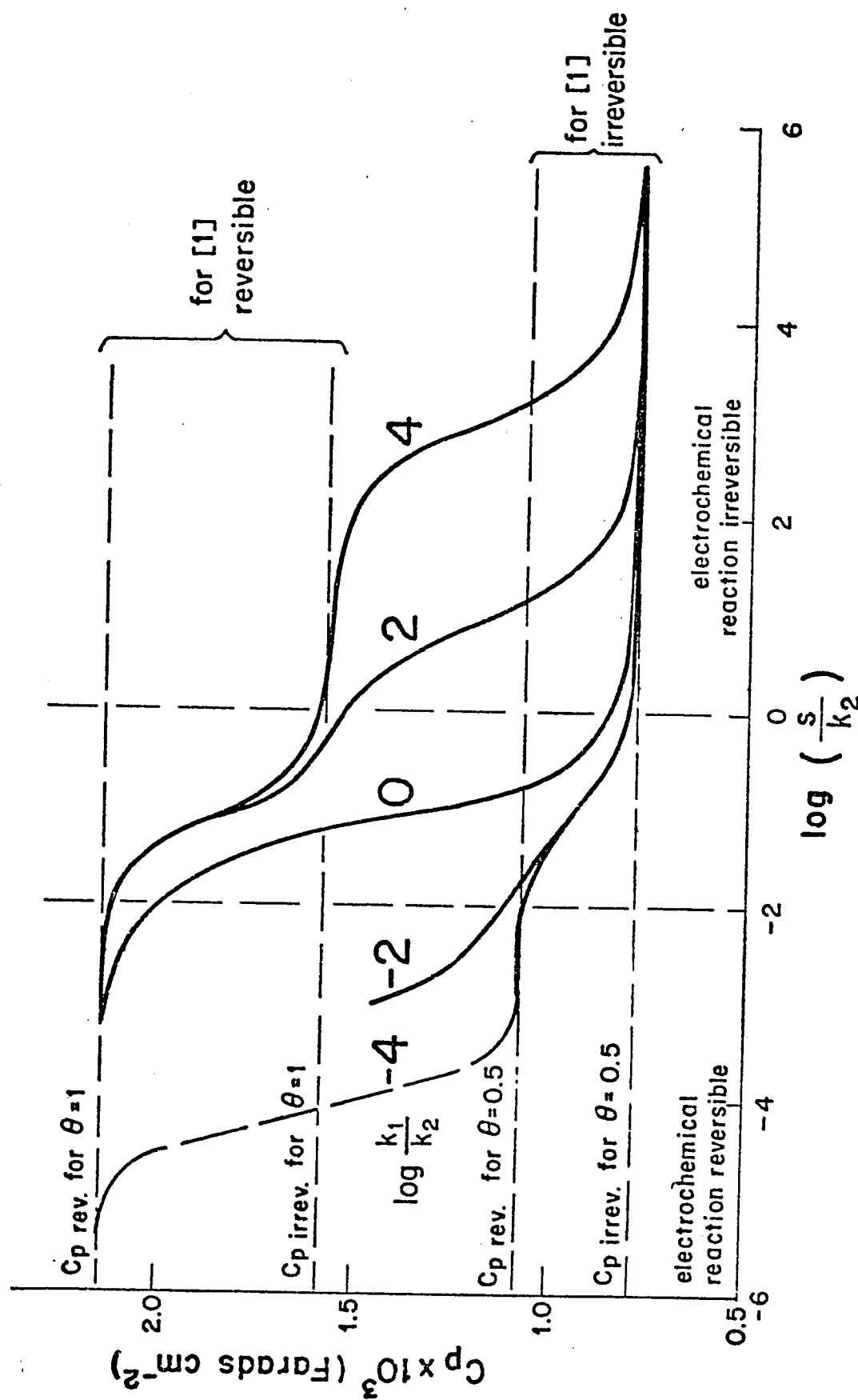


Fig. 6-3 Family of plots of C_p for reaction mechanism (III) as a function of $\log \frac{s}{k_2}$ for various $\log \frac{k_1}{k_2}$ values (from -4 to +4); $k_1 = k_{-1}$ is taken, corresponding to $\theta_{B, \text{in}} = 0.5$.

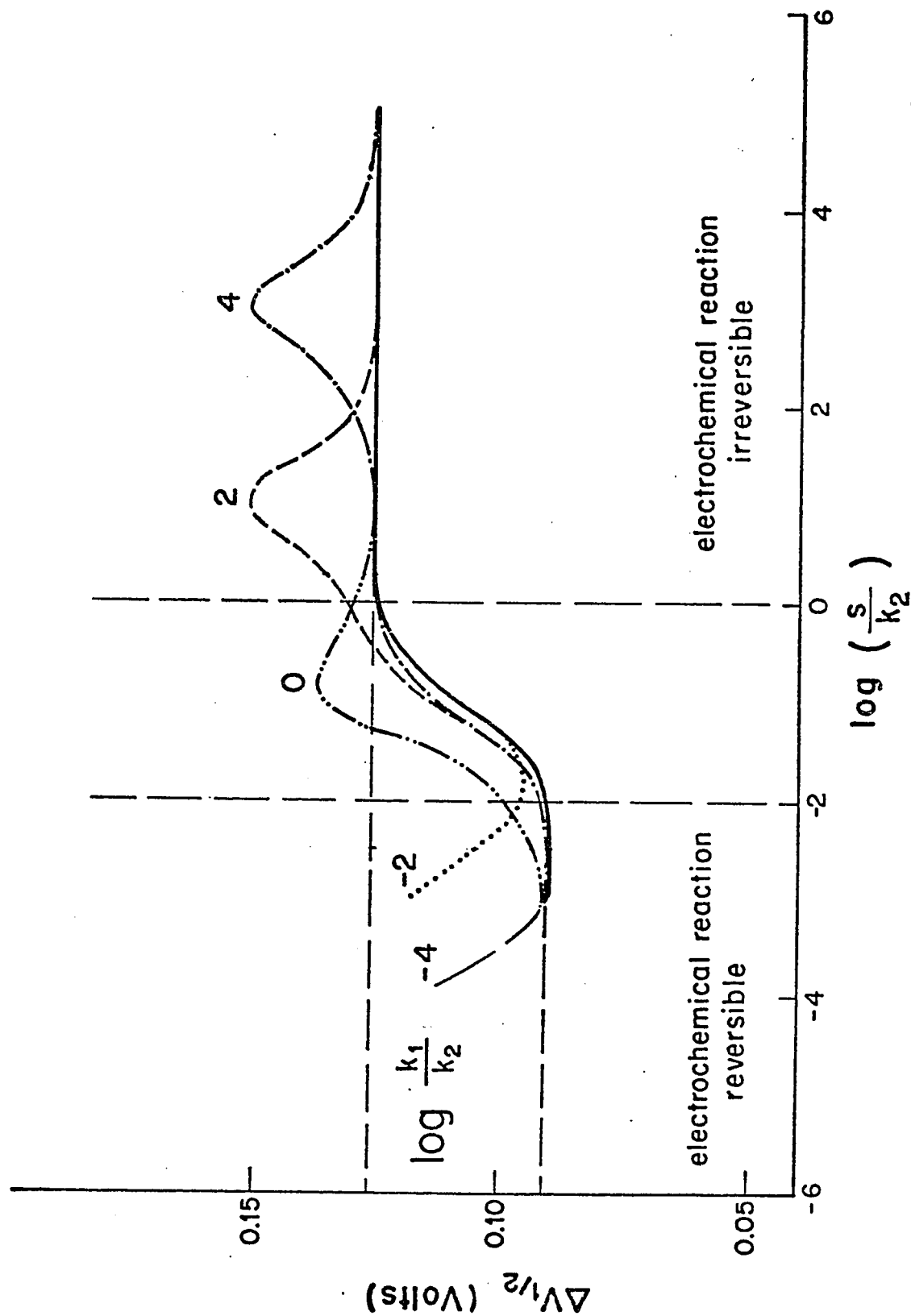


Fig. 6-4 Plots of half-widths, $\Delta V_{1/2}$, as a function of $\log \frac{s}{k_2}$ for various values of $\log \frac{k_1}{k_2}$ (from -4 to +4) for reaction mechanism (III); $k_1 = k_{-1}$ is taken, corresponding to $\theta_{B,in} = 0.5$.

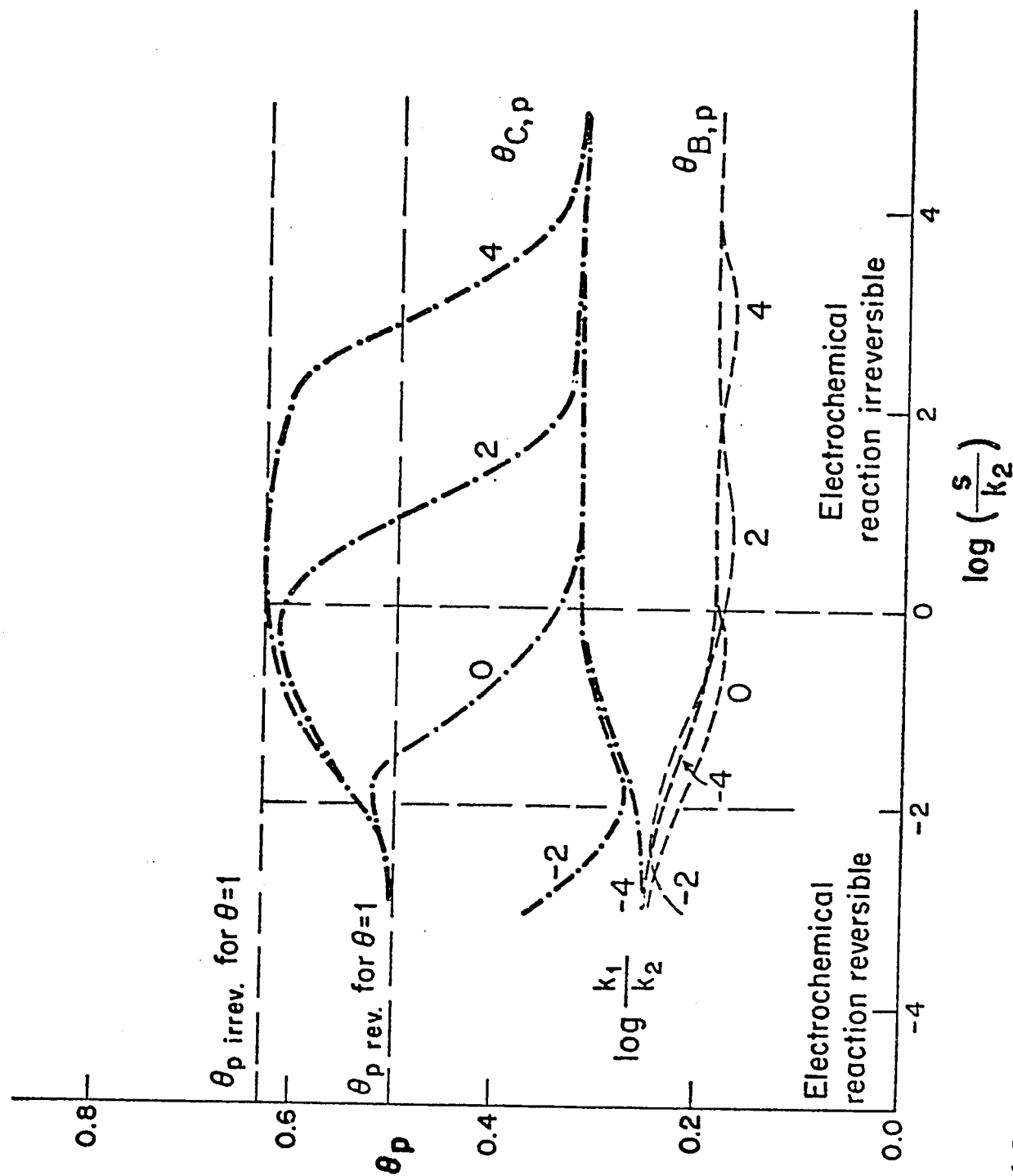


Fig. 6-5 Dependence of coverage θ_p to the peak by species B and C in reaction mechanism (III) on $\log \frac{s}{k_2}$ for various $\log \frac{k_1}{k_2}$ ratios (from -4 to +4); $k_1 = k_{-1}$ is taken, corresponding to $\theta_{B,in} = 0.5$.

of the C-V profiles for these conditions and the ratio of $C_{p,rev.}/C_{p,irrev.}$, if both $C_{p,rev.}$ and $C_{p,irrev.}$ can be obtained for the same k_1/k_2 ratio, will remain the same as for reaction (I).

The kinetic parameters for reaction [2] [case (b)] can be found in the usual way, as for reaction (I), from the plot of V_p vs. $\log s$. Only E_2° for reaction sequence (III), which will not be equal to $V_{p,rev.}$, as it is for reaction (I), has to be derived independently from $(V_{p,a} - V_{p,c})/2$, where $V_{p,a}$ and $V_{p,c}$ are the anodic and cathodic peak potentials, respectively. For reaction [1], kinetic information can be obtained by following the rate of generation of species B in step [1] before a sweep is applied. This would be achieved by measuring the area under the i-V profile resulting from a fast sweep applied after some controlled time during which species B is formed. From the equilibrium value of θ_B , the equilibrium constant for step [1] can be evaluated.

Another important and characteristic feature of the kinetic behaviour of reaction scheme (III) is that, in case (b), holding the potential constant will increase the overall cathodic currents throughout the following reverse sweep, as well as $i_{p,c}$ due to adjustment of the coverage θ_B in step [1] (see Fig. 6-7). Useful data can thus be obtained from holding experiments.

When steps [1] and [2] have comparable rates, the above mentioned, unusually broad C-V profiles arise corresponding (Fig. 6-2a, curve for $\log \frac{s}{k_2} = 1$; Fig. 6-2b for $\log \frac{s}{k_2} = -1$ and Fig. 6-2c for

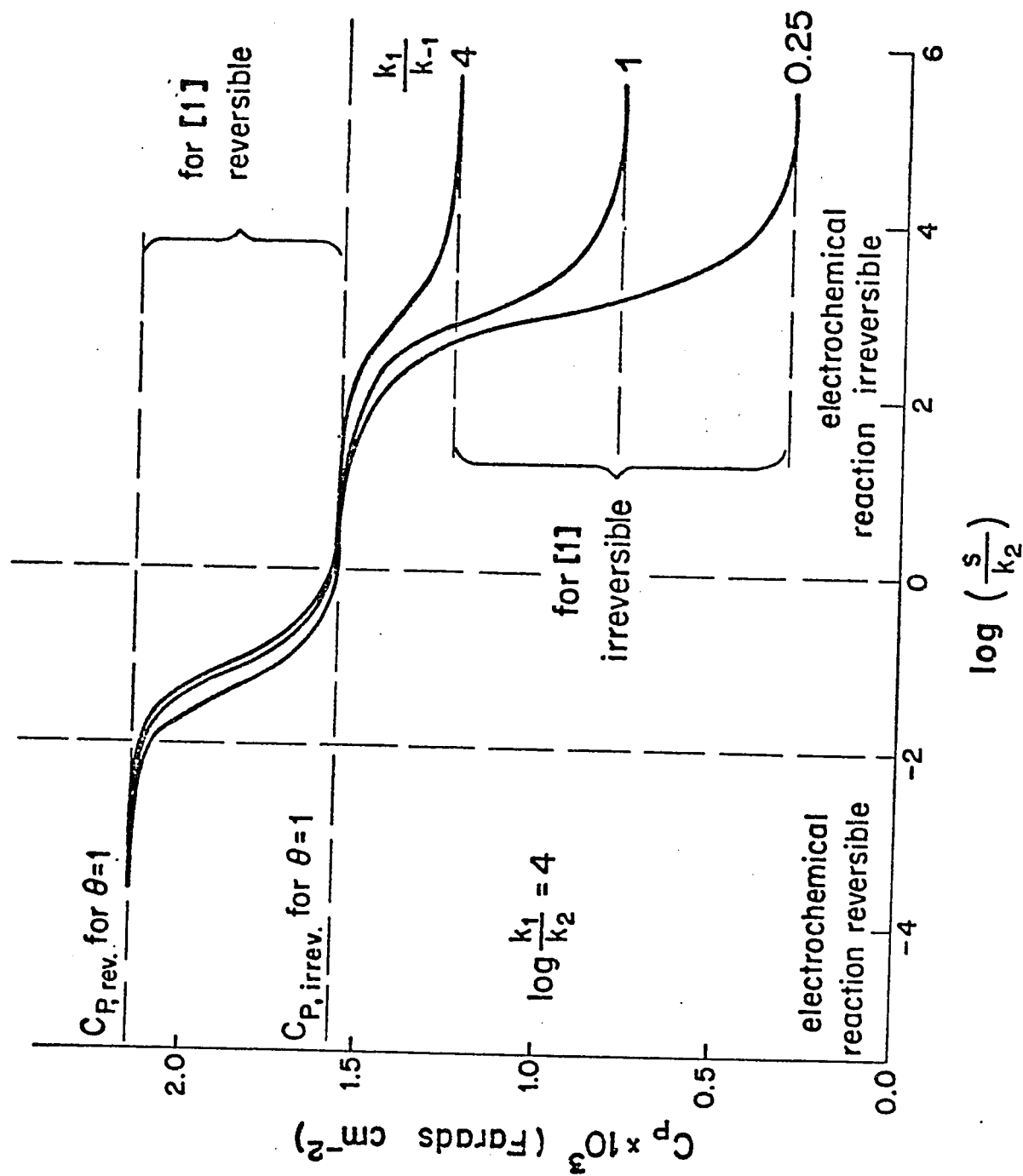


Fig. 6-6 Family of plots of C_p for reaction sequence (III) as a function of $\log \frac{s}{k_2}$ for $\log \frac{k_1}{k_2} = 4$ and for various ratios of k_1/k_{-1} (4, 1, 0.25) corresponding to $\theta_{R,in}$ equal to 0.8, 0.5 and 0.2, respectively.

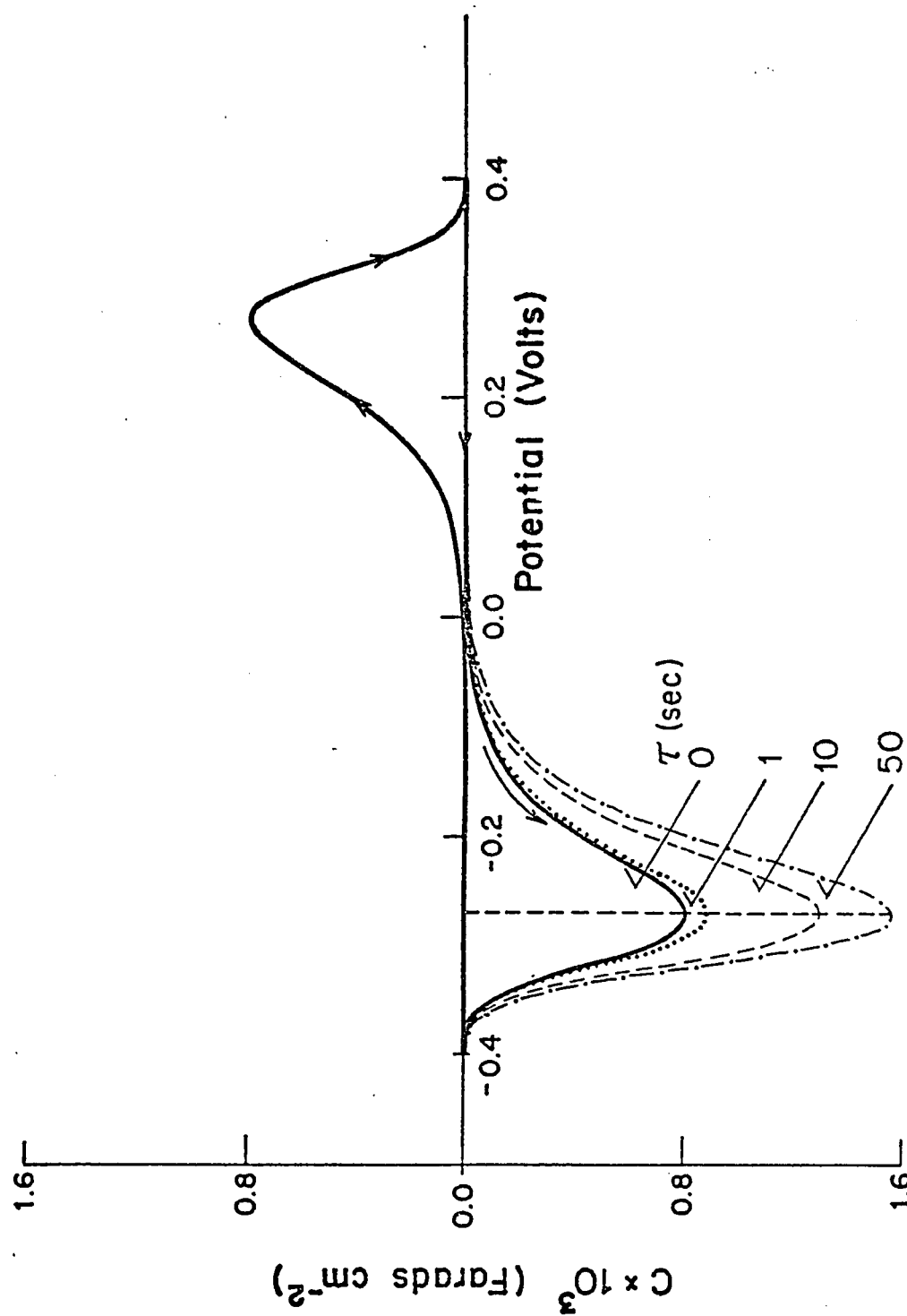


Fig. 6-7 The effect of holding the potential constant at the end of the anodic sweep on the following cathodic C-V profile for various holding times, τ , when the chemical step [1] of reaction sequence (III) behaves irreversibly during continuous sweeping. ($V_h = 0.4$ Volts, $\frac{k_1}{k_2} = 1$ and $\log \frac{s}{k_2} = 1$).

$\log \frac{s}{k_2} = -3$) to the maxima in $\Delta V_{1/2}$ shown in Fig. 6-4 and minima of $\theta_{B,p}$ (Fig. 6-5). This effect arises because an increasing quantity of B, electroactive in reaction [2], is generated during the time of the sweep and converted in reaction [2] to chemisorbed species C. This produces the broadness of the peak and the tail on the C-V profile which eventually becomes the limiting current, i_{Lim} , referred to above as is well illustrated in Fig. 6-2b, curve for $\log \frac{s}{k_2} = 0$. From the limiting current, the rate constant k_1 can be readily evaluated. As in the case of step [1] being completely irreversible, holding the potential at the end of the anodic sweep gives larger peaks on the reverse sweep due to accumulation of species B at a rate equivalent to the chemically controlled limiting current of reaction [1].

The value of maximum half-width, $\Delta V_{1/2}$, depends on the initial coverage of the surface by species B and increases as the initial value of θ_B becomes smaller (Fig. 6-8). This variation of $\Delta V_{1/2}$ is not to be confused with that discussed in Chapter IV, where it was shown (cf. also ref. 93) how the half-width of peaks for reaction (I) is determined by the interaction parameter g . In fact, the broad peak observed for this reaction sequence has a quite different shape from that caused by lateral interactions in the adsorbed layer, as can be seen from a comparison of Fig. 6-12 with Figs. 4-5a,b in Chapter IV. Due to the change of θ_B during the sweep, or on holding the potential constant, when production of B is controlled by the limiting reaction current for step [1], the family of C-V profiles for the reversed sweep will not be 180°-rotated images of the forward-sweep C vs. V profiles

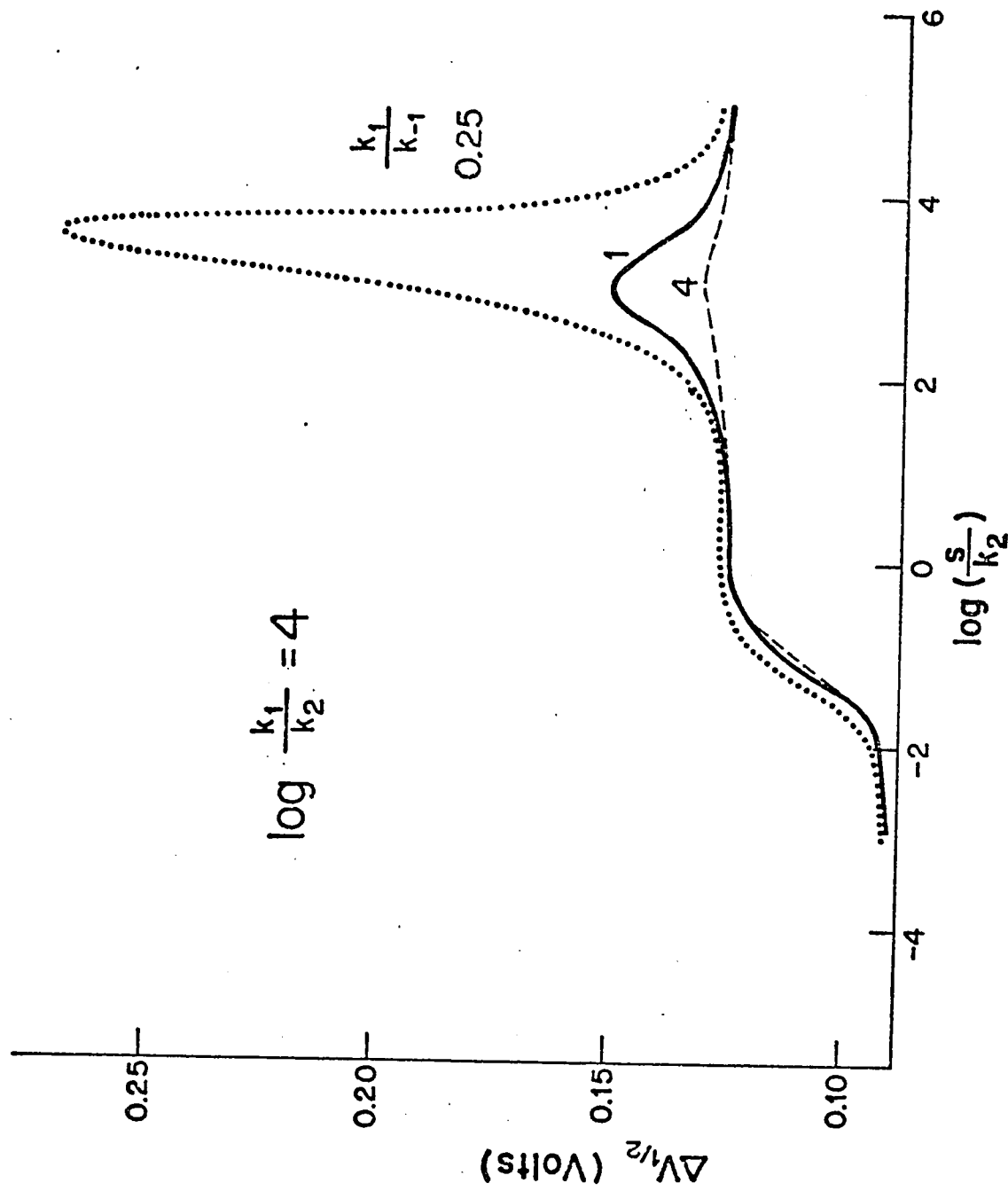


Fig. 6-8 Plots of half-widths, $\Delta V_{1/2}$, of the C-V profiles for reaction mechanism (III) as a function of $\log \frac{s}{k_2}$ for $\log \frac{k_1}{k_2} = 4$ and for various values of k_1/k_{-1} (4, 1, 0.25) corresponding to $\theta_{B,in}$ equal to 0.8, 0.5

(compare Figs. 6-1 and 6-2). The case of a totally irreversible chemical reaction [1] is the only exception; then, the backward reaction [2] in reaction sequence (III) proceeds as in the simple 1-e electrochemical reaction (I) but with all currents proportional to the value of θ_B established initially.

6.5 Reaction Sequence (IV)

6.5.1 Formulation of kinetic equations

The kinetic equations used for computation of the C-V profiles for this reaction sequence (IV) were:

$$\begin{aligned} \frac{d\theta_B}{dt} = & k'_{IV,1} c_A (1-\theta_B) - k_{IV,-1} \theta_B - k_{IV,2} \theta_B \exp\left(\frac{\Delta V}{b}\right) + \\ & k'_{IV,-2} c_C (1-\theta_B) \exp\left(-\frac{\Delta V}{b}\right) \end{aligned} \quad (6-6)$$

and

$$i = F \frac{dc_C}{dt} = F \left\{ \frac{Q}{F} [k_{IV,2} \theta_B \exp\left(\frac{\Delta V}{b}\right) - k'_{IV,-2} c_C (1-\theta_B) \exp\left(-\frac{\Delta V}{b}\right)] \right\} \quad (6-7)$$

where the rate constant, concentration and coverage symbols are self-explanatory.

The initial conditions ($t=0$) were: $\theta_{B,in}$ equal to its equilibrium value for reaction [1] which, for the rate constant ratio chosen, corresponds to 0.5. The starting potential V_{in} was selected so that the equilibrium coverage would not be modified, i.e., $V_{in} = E_2^\circ$.

6.5.2 General characteristics of reaction mechanism (IV)

For reaction sequence (IV), the following characteristic features (Figs. 6-9 and 6-10), dependent on the rate constants k_1 , k_2 and sweep-rate s , can be observed:

- (i) as long as the electrochemical step is rate-determining and s/k_2 is small, no current peak is developed in i - V profiles (Fig. 6-9, curve for $\log \frac{s}{k_2} = -2$ and Fig. 6-10). Under these conditions, the current increases and the coverage by the product B of step [1], diminishing slowly, reaches a steady-state value at all potentials until the i_{Lim} is attained (Figs. 6-9 and 6-10). A Tafel line with a slope of 0.118V may be constructed (Fig. 6-10) from which the kinetic parameters i_0 and α of reaction [2] can be calculated in the usual way. The rate constant k_1 can then be obtained from the limiting current: $i_{Lim} = Q k_1$, where $k_1 = k'_1 c_A$.
- (ii) peaks are observed (Figs. 6-9 and 6-10) when s/k_2 makes the rate of step [2] comparable with that of the chemical reaction [1], i.e., as the latter is becoming rate-controlling; however, the same i_{Lim} is eventually attained at high potentials. The current maximum arises because values of θ_B , higher than the ultimate steady-state value, initially exist during the sweep for certain values of the rate constants and s/k_2 ratio. Behaviour of this kind is observed experimentally in oxidation of HCOOH under anhydrous conditions¹⁴⁶.
- (iii) as in reaction sequence (III), when s/k_2 is sufficiently

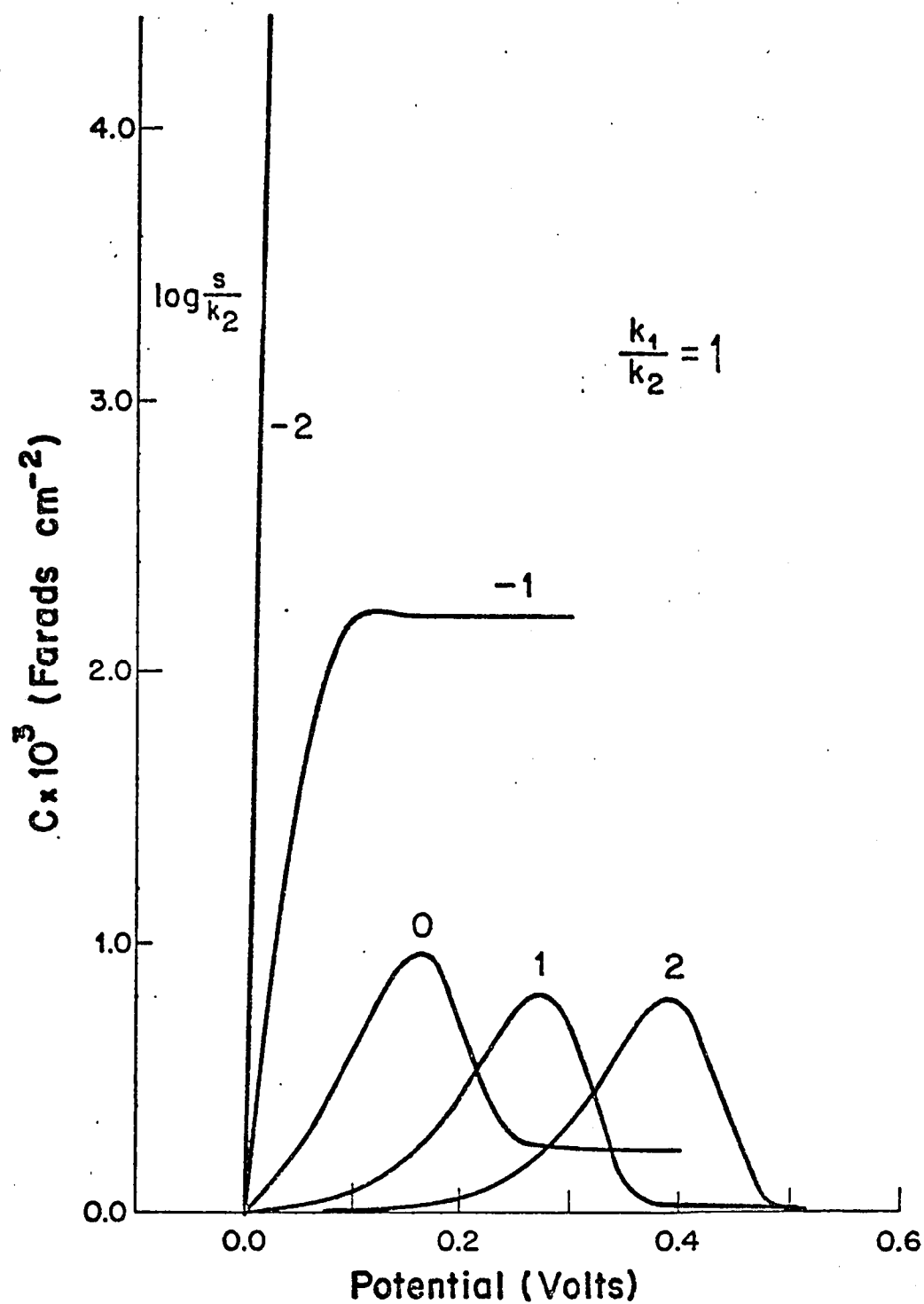


Fig. 6-9 Anodic C vs. V profiles for reaction mechanism (IV) for various s/k_2 values and for $\frac{k_1}{k_2} = 1$; $k_1 = k_{-1}$ is taken, corresponding to $\theta_{B,in} = 0.5$.

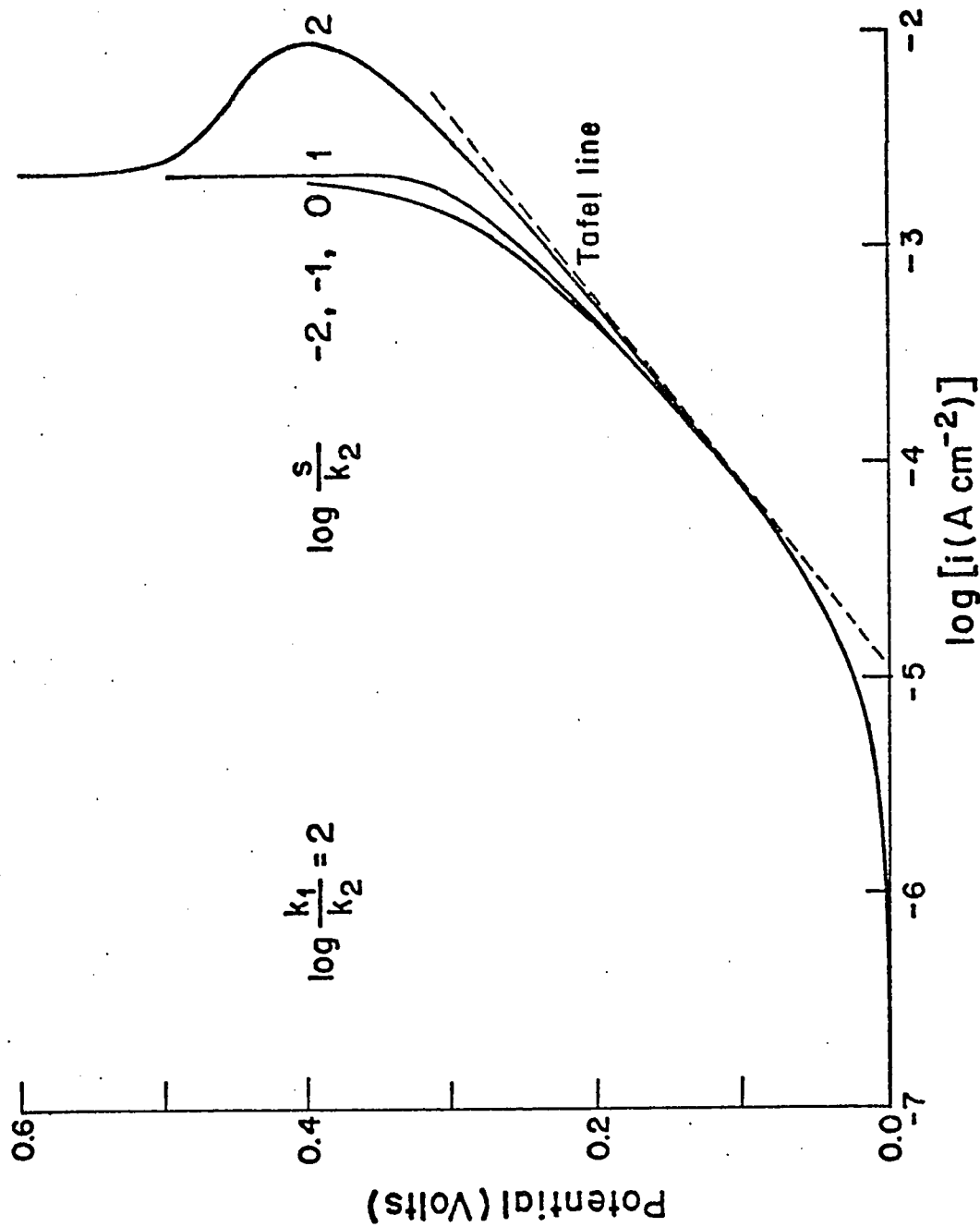


Fig. 6-10 Polarization curves (V vs. $\log i$) for reaction sequence (IV) for various $\log \frac{s}{k_2}$ values and for $\log \frac{k_1}{k_2} = 2$.

large that the chemical reaction [1] of sequence (IV) has no time to supply B species for reaction [2] during the sweep, a C vs. V profile, for step [2] behaving as an isolated 1-e reaction with pseudocapacitance C values depending on the initial θ_B values, can be obtained (Fig. 6-9; curves for $\log \frac{s}{k_2} = 1$ and 2). Then, for this case, (a) the kinetic parameters for reaction [2] and (b) the equilibrium constant K_{IV} for reaction [1] can be obtained as in the case of sequence (III).

6.6 Reaction Sequence (V)

6.6.1 Formulation of kinetic equations

The following kinetic equations were used for computation of the C-V profiles for reaction sequence (V):

$$\frac{d\theta_B}{dt} = k'_{V,1} c_A (1-\theta_B-\theta_C) \exp\left(\frac{\Delta V}{b}\right) - k_{V,-1} \theta_B \exp\left(-\frac{\Delta V}{b}\right) -$$

$$k_{V,2} \theta_B - k_{V,-2} \theta_C \quad (6-8)$$

and

$$\frac{d\theta_C}{dt} = k_{V,2} \theta_B - k_{V,-2} \theta_C \quad (6-9)$$

the current being taken as

$$i = Q[k'_{V,1} c_A (1-\theta_B-\theta_C) \exp\left(\frac{\Delta V}{b}\right) - k_{V,-1} \theta_B \exp\left(-\frac{\Delta V}{b}\right)] \quad (6-10)$$

For $t=0$, the initial coverages θ_B and θ_C were always taken as 0.

6.6.2 Features of current-potential profiles obtained for sequence (V)

For conditions under which the electrochemical reaction [1] is rate-determining with step [2] in equilibrium, so that during the sweep θ_B always maintains its equilibrium value, the anodic and cathodic sweep will generate C-V profiles corresponding to the respective profiles for reaction (I). With reaction [2] totally irreversible, so that, during the time of the sweep, no change in the maximum attainable coverage by B occurs, a C-V profile for the reaction mechanism (V), similar to that for the 1-e electrochemical reaction (I), will be obtained but the values of pseudocapacitance C will be proportional to whatever value of $1-\theta_C$ exists initially. Kinetic information can then be obtained for reaction [1] in the usual way (see Chapter IV).

For reaction [2], kinetic information can only be obtained when the rates of reactions [1] and [2] are comparable. Under these conditions, in the forward sweep only, a very slight influence of reaction [2] can be observed in the reversible or nearly reversible peak which, due to transformation of species B into C during the sweep, will become slightly higher and narrower, e.g., for $\frac{k_1}{k_2} = 100$, $C_p = 2.23 \times 10^3 \mu F \text{ cm}^{-2}$ and $\Delta V_{1/2} = 87 \text{ mV}$ instead of $C_p = 2.14 \times 10^3 \mu F \text{ cm}^{-2}$ and $\Delta V_{1/2} = 90 \text{ mV}$ as expected for reaction (I). No changes can be observed in the irreversible peaks and the differences in the forward sweep behaviour are too small to be indicative of the mechanism. Therefore, no information on reaction sequence (V) can be derived from

anodic sweeps alone. Features which indicate that an "ec" mechanism is involved arise from the behaviour in the backward direction of the sweep which is analogous to that for the forward sweep in reaction sequence (III). In the backward sweep, the unusually broad peak which exhibits tailing of the current as the potential progresses in the sweep, as seen also in reaction sequence (III), can be observed (Fig. 6-11, cathodic curve for $\log \frac{s}{k_1} = -1$) as well as a limiting current (Fig. 6-11, cathodic curve for $\log \frac{s}{k_1} = 0$). In Fig. 6-11, the ratio k_1/k_2 is taken as 1 but similar families of C-V profiles may be obtained for different k_1/k_2 ratios. The shape of the broad peak depends, as in the case of reaction sequence (III), on $\theta_{B,in}$ (Fig. 6-12).

It should be pointed out that if the rates of reactions [1] and [2] are comparable, multiple sweeps will change both the anodic and cathodic C-V profiles until the same quantity of species C, formed from species B in the anodic-going sweep, is converted back to species B in the cathodic-going sweep; this applies when both anodic and cathodic potential limits are kept at arbitrary but constant values. A similar effect arises for reaction sequence (III), as was noted in Section 6.4.2.

Indication that an "ec" mechanism is involved can also be obtained, of course, from experiments in which the potential is held at the end of an anodic sweep. Under conditions where the chemical step [2] is no longer reversible, holding will decrease the overall cathodic (reverse) sweep currents, as well as the cathodic i_p , due to conversion of electroactive species B to C. This is in contrast to scheme (III) where holding increases the currents in the reverse sweep.

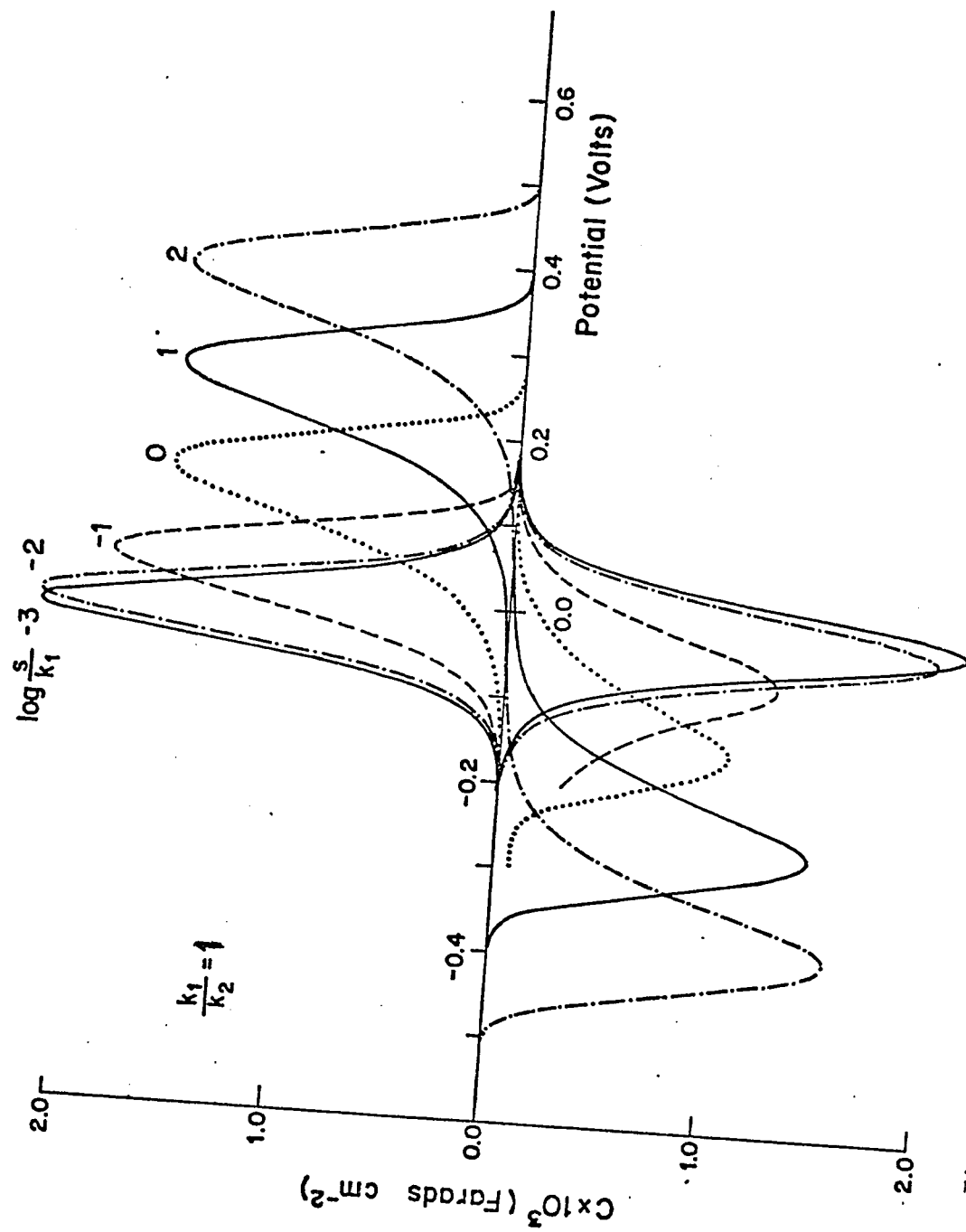


Fig. 6-11 Anodic and cathodic C-V profiles for reaction sequence (V) for various $\log \frac{s}{k_1}$ values showing progression from reversible to irreversible behaviour of step [1] for k_1/k_2 values taken equal to 1.

In order to be able to use such effects quantitatively, the cathodic sweep has to be fast enough to make reaction step [2] irreversible so that no species B is formed during the sweep from species C (which is itself formed during holding). Kinetics of the reaction sequence (V) can then be derived from these holding experiments by means of a plot of $\log \frac{di_{p,\tau}}{d\tau}$ vs. time of holding τ ; thus, the values of k_2 and k_{-2} can be determined from its slope

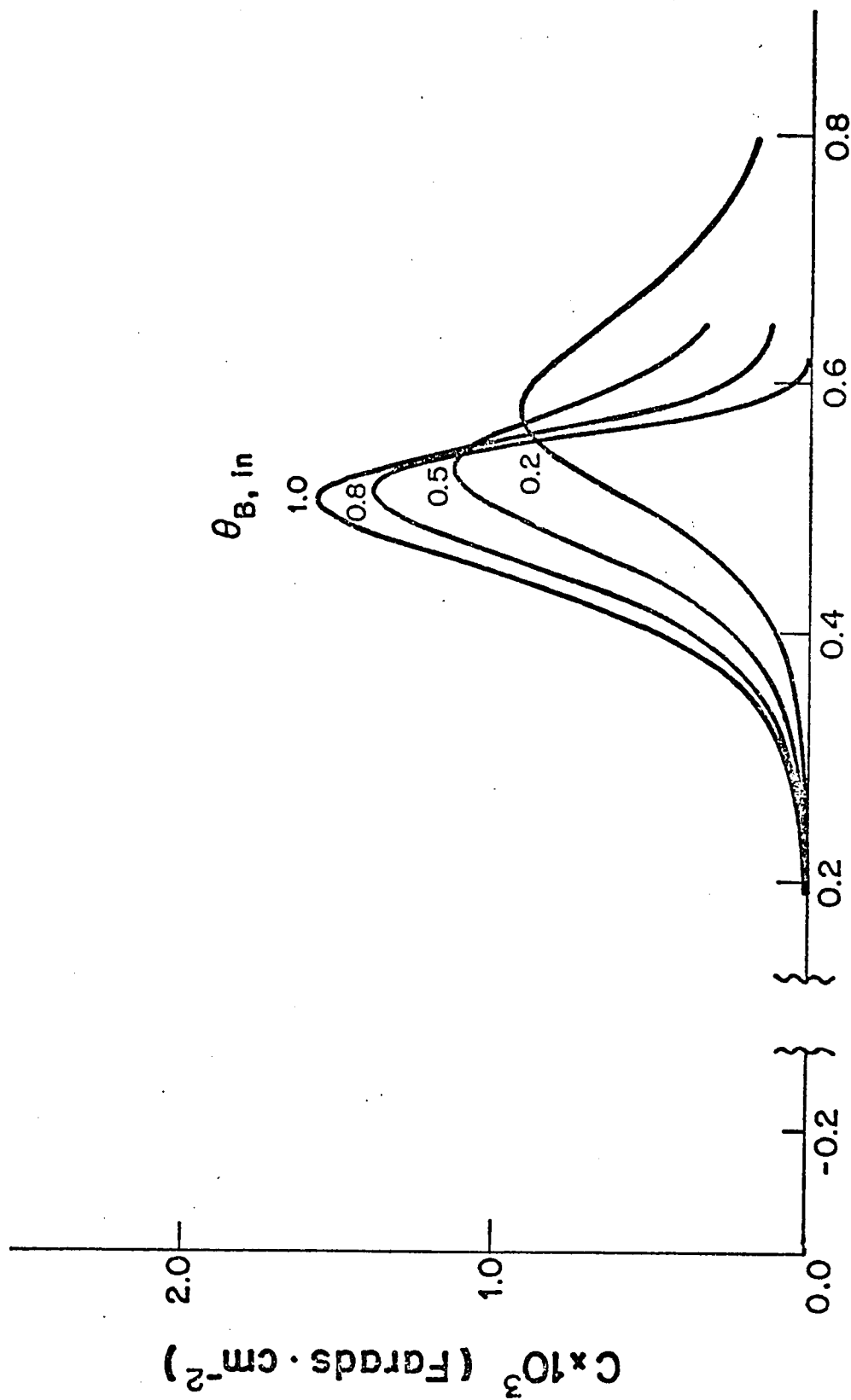
$$[= -(k_2 + k_{-2})/2.303]$$

and its intercept

$$[= \log (|i_{p,\tau=0}| \cdot k_2)] .$$

The value of E_1° is obtained as previously described for reaction sequence (III). From E_1° , $V_{p,a}$ and s , the values of k_1 ($k'_1 = k_{-1}$) may then be calculated provided that the electrochemical step [1] is driven at sufficiently high s to behave irreversibly. $k_{V,2}$ can also be obtained, as $k_{III,1}$ in reaction mechanism (III), from the limiting current observed (Fig. 6-11, cathodic curve for $\log \frac{s}{k_{V,1}} = 0$).

It is to be noted that a step such as [2] is involved in the place-exchange process^{65,102} in the oxidation of noble metal⁶⁶ but the conversion of C to A can proceed by a different pathway, thus leading the hysteresis^{66,102}. The place-exchange process and the equations which govern it will be discussed in detail in Chapter VIII.



Potential (Volts)

Fig. 6-12 Comparison of the shape of an irreversible C-V curve for reaction (I) for $g=0$ (curve for $\theta_{B,in} = 1.0$) with the broad curve for the cathodic reaction [1] in sequence (V) for $\log \frac{s}{k_1} = 4$, for $\log \frac{s}{k_1} = 3$ and for various k_2/k_{-2} ratios corresponding to $\theta_{B,in} = 0.8, 0.5, 0.2$. (An equivalent behaviour arises for reaction mechanism (III) in the anodic direction).

6.7 Summary of Characteristic Features of the C-V Profiles of a Surface Reaction in which a First-Order Chemical Step is Coupled with an Electrochemical One

From the C vs. V profiles of Figs. 6-2, 6-9 and 6-11, a number of characteristic features of the kinetic behaviour of the reaction sequences (III), (IV) and (V) may be derived and compared with those of reaction (I). This will allow classification of an unknown reaction mechanism into the above scheme. An attempt should always be made to obtain, by changing the sweep-rate, a series of characteristic C-V profiles ranging from reversible to irreversible behaviour of the reaction. By analysis of the dependence of the main parameters C_p , $\Delta V_{1/2}$ and V_p on $\log s$, the appropriate reaction scheme can then be assigned and the conditions, which enable calculation of the kinetic parameters to be made, can be selected.

The following are the general features which indicate the presence of a complex reaction mechanism:

- (i) Different anodic and cathodic C vs. V profiles are observed;
- (ii) Changes of the sweep profile with holding time can arise, depending on conditions;
- (iii) Reversible peak potential $V_{p,rev} \neq E^\circ$ for the electro-chemical step, even though the interaction parameter $g = 0$.

Features of individual reaction schemes are:

- (a) Reaction sequence (III)
 - (i) Pseudocapacitance peaks always arise.

- (ii) A small limiting current can arise when both the electrochemical and chemical steps have comparable rates.
- (iii) Peaks of unusually low aspect-ratio arise for the conditions in (ii), corresponding to a maximum in the $\Delta V_{1/2}$ vs. $\log \frac{s}{k_2}$ plot.
- (iv) Holding increases pseudocapacitance values throughout the reverse sweep.

(b) Reaction sequence (IV)

- (i) A Tafel region is generated in the i-V profile.
- (ii) A chemical reaction limited current always appears.
- (iii) Pseudocapacitance peaks arise only when the chemical step is irreversible.

(c) Reaction sequence (V)

- (i) Pseudocapacitance peaks always arise.
- (ii) The C-V profiles of the reverse sweep but not the forward sweep are characteristic of this mechanism and exhibit a low aspect-ratio peak and a limiting current.
- (iii) Holding diminishes currents in the reverse sweep when the chemical reaction is irreversible.

CHAPTER VII

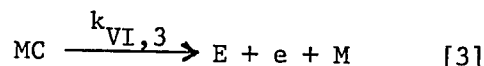
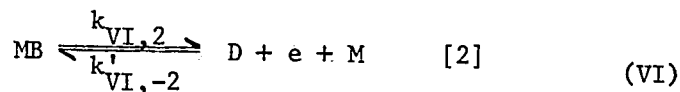
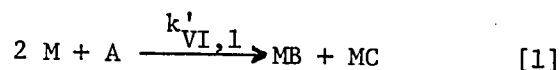
SIMULATION OF KINETIC BEHAVIOUR OF A COMPLEX REACTION (THREE STEPS) INVOLVING DISSOCIATIVE CHEMISORPTION

7.1 Introduction

The model case of a "ce" mechanism described in the previous chapter (VI) for reaction sequence (IV) is extended to a more complex reaction sequence. A dissociative chemisorption step followed by two parallel electrochemical reactions, of which one is assumed to be completely reversible and the other irreversible, will be considered in the present chapter.

This type of reaction mechanism is a very realistic one, for it can arise in electro-oxidation of H_2 (cf. ref. 98) and simple organic molecules on metal surfaces which can act as catalysts. An example is an organic molecule $HOrg$, soluble in aqueous medium, which adsorbs on the electrode surface and dissociates into H_{ads} and Org_{ads} . It should be pointed out that the dissociated adsorbed hydrogen is not necessarily the acidic hydrogen atom in a case such as $HCOOH$ but can be another one originating from other functional groups. The organic part of such a molecule could then be oxidized irreversibly and leave the surface forming a water soluble product (CO_2 in the case of $HCOOH$, CH_3OH , etc.). Adsorbed hydrogen produced in the chemisorption step can be electrochemically desorbed ($H_{ads} \rightleftharpoons H_{aq}^+ + e$) reversibly from the surface, depending on the applied potential, as is well known^{47-49,59}.

For the purposes of kinetic simulation, it is assumed that a species A in solution first becomes dissociatively adsorbed on to free metal sites M, producing chemisorbed species B and C (reaction [1], below), at coverages θ_B and θ_C , respectively. These two species are then regarded as undergoing electrochemical oxidations to solution-soluble species D and E^{*}, respectively, with different rates and thus free surface sites are regenerated. These electrochemical oxidations are represented by reactions [2] and [3], respectively (see below). Hence the overall reaction mechanism can be represented as follows:



It is assumed that the backward rate constants for the dissociative chemisorption step [1] and electrochemical oxidation of adsorbed species C to the solution-soluble species E (reaction [3]) are much smaller than their respective forward rate constants, so that the two reactions are assumed to behave irreversibly. Electrochemical oxidation of the adsorbed species B to the solution-soluble species D is assumed to proceed in a completely reversible way with forward and backward rate constants taken for convenience as equal, i.e.,

* Here the letter E stands for a chemical species, soluble in solution and should not be confused with letters E° representing the standard electrode potentials of electrochemical reactions in question.

$k_{VI,2} = k'_{VI,-2}$. An example of this type of step is desorptive oxidation of adsorbed H in many electrocatalytic oxidations.

7.2 Calculation Procedure and Values of Parameters

The results were again obtained by numerical methods using the computer simulation technique with "System/360 Continuous System Modeling Program" - (S/360 CSMP). The standard Runge-Kutta fourth-order, variable step integration method, discussed in detail in Chapter III, was used in the simulations, as for all other reaction mechanisms.

The standard electrode potentials E_2° and E_3° for the electrochemical surface processes (reactions [2] and [3]) were chosen (see Part 7.4) to be 0.0 V and -0.2 V, respectively. The solution concentrations c_A and c_D of soluble species A and D were taken as 1 mol l^{-1} and concentration, c_E , of species E in solution, was assumed to be so small and not changing during the reaction (consider, e.g., dissolved CO_2 gas) that, in effect, the backward rate of reaction [3] can be neglected. No diffusion limitations in any of the above reaction steps were considered in the present work. Both chemisorbed species B and C were assumed to follow Langmuir isotherms, even though criteria could be developed for cases where interaction effects ($g \neq 0$) are significant. The charge to form a monolayer by either the species B or C was taken as $220 \text{ } \mu\text{C cm}^{-2}$, for convenience, but in a real system this assumption may or may not apply. However, selection of an appropriate value is always easy. The symmetry factor β was again taken as 0.5.

7.3 Formulation of Kinetic Equations

For reaction mechanism (VI), the total current density as a function of potential V in the sweep at a sweep-rate $s = \frac{dV}{dt}$ is the sum of i_2 , the current density for reaction [2], and i_3 , the current density for reaction [3], i.e.,

$$i_{\text{Tot}} = i_2 + i_3 \quad (7-1)$$

The individual currents may be written as

$$i_2 = F \frac{dc_D}{dt} = F \left\{ \frac{Q}{F} [k_{\text{VI},2} \theta_B \exp(\frac{\Delta V_2}{b}) - k'_{\text{VI},-2} c_D (1-\theta_B-\theta_C) \exp(-\frac{\Delta V_2}{b})] \right\} \quad (7-2)$$

and

$$i_3 = F \frac{dc_E}{dt} = F \left[\frac{Q}{F} k_{\text{VI},3} \theta_C \exp(\frac{\Delta V_3}{b}) \right] = Q k_{\text{VI},3} \theta_C \exp(\frac{\Delta V_3}{b}) \quad (7-3)$$

where the modulating potentials for individual electrochemical reactions are:

$$\Delta V_2 = V - E_2^\circ = V_{\text{in}} \pm st - E_2^\circ \quad (7-4)$$

$$\Delta V_3 = V - E_3^\circ = V_{\text{in}} \pm st - E_3^\circ \quad (7-5)$$

V_{in} is the initial potential in the sweep and $b = \frac{2RT}{F}$ (for $\beta = 0.5$). The value of V_{in} was chosen to be sufficiently negative relative to the standard electrode potential, E_2° , corresponding to the reversible electrochemical reaction [2], that the chemisorption equilibrium previously established in step [1] and/or [2] remained practically unchanged. The V_{in} value was taken as -0.2 V for computational convenience only.

The coverages θ_B and θ_C in eqns. (7-2) and (7-3) were obtained by integration from the following equations:

$$\frac{d\theta_B}{dt} = k'_{VI,1} c_A (1-\theta_B-\theta_C)^2 - k_{VI,2} \theta_B \exp\left(\frac{\Delta V_2}{b}\right) + k'_{VI,-2} c_D (1-\theta_B-\theta_C) \exp\left(-\frac{\Delta V_2}{b}\right) \quad (7-6)$$

and

$$\frac{d\theta_C}{dt} = k'_{VI,1} c_A (1-\theta_B-\theta_C)^2 - k_{VI,3} \theta_C \exp\left(\frac{\Delta V_3}{b}\right) \quad (7-7)$$

Two sets of initial conditions were considered:

$$(a) \quad \theta_{B,in} = 1.0 \quad \text{and} \quad \theta_{C,in} = 0.0$$

$$(b) \quad \theta_{B,in} = 0.5 \quad \text{and} \quad \theta_{C,in} = 0.5$$

7.4 Effect of Applied Sweep-Rate on the Current-Potential Profiles

In order to obtain the current-potential curves for the two cases (a) and (b) discussed below, such that they partly or completely overlap, it is necessary to choose the rate constants k'_1 and k_3 appropriately. It was found that the i - V curves depend not only on the external variable s , but on the ratio k_1/k_3 and the E_3° value as well. For different values of E_3° , different k_1/k_3 ratios and/or different sweep-rate ranges are required to produce i - V profiles in which the characteristic features of the behaviour of this reaction scheme are demonstrated. Since, in the present calculations, the value of the standard electrode potential E_3° was taken as constant (see Part 7.2), it was found that the ratio $\frac{k_1}{k_3} = 100$ gave good resolution of the two electrochemical processes [2] and [3] of this reaction

mechanism (VI). It should be pointed out, however, that the absolute values of k_1 and k_3 depend on the sweep-rate range employed, because for a peak to appear at a given potential V referred to E_3° , the ratio s/k_3 must be constant.

7.4.1 Initial conditions - Case (a)

When the initial condition (a) prevails (see p.142), i.e., when the surface is completely covered by species B at the beginning of the sweep, the following characteristic features (Figs. 7-1 and 7-2) are observed:

- (i) For sufficiently small values of $\log \frac{s}{k_3}$, no peak in the i - V (or C - V) profile can be seen (e.g., Figs. 7-1 and 7-2 for $\log \frac{s}{k_3} = 0$) and current increases continuously until a reaction limiting current, i_{Lim} , is reached. As the sweep-rate increases, the peak corresponding to the reversible electrochemical reaction [2] starts to appear but the peak corresponding to reaction [3] behaving irreversibly is still not observed because the chemical process [1] is still faster than reaction [3]. Again, only a plateau corresponding to the value of i_{Lim} , which cannot exceed the rate of the dissociative chemical reaction [1], appears (Figs. 7-1 and 7-2 for $\log \frac{s}{k_3} = 1$). With further increase of sweep-rate, the second peak corresponding to the process [3] is observed (Figs. 7-1 and 7-2 for $\log \frac{s}{k_3} = 2$). The pseudocapacitance peak will shift and decrease in height with additional

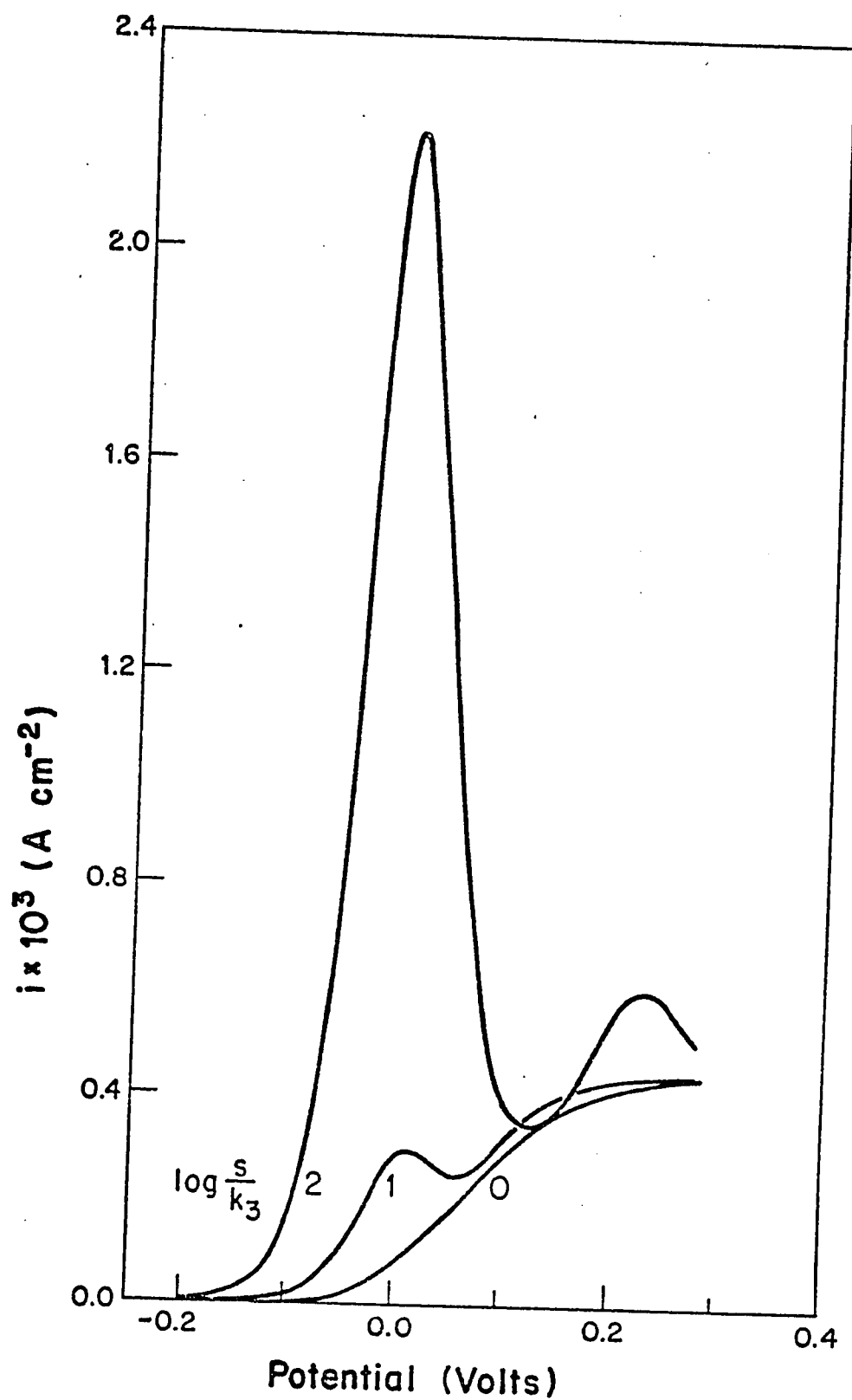


Fig. 7-1 Series of i - V profiles for reaction sequence (VI) for various s/k_3 values. $E_2^\circ = 0.0$ V, $E_3^\circ = -0.2$ V, $\frac{k_1}{k_3} = 100$.
Initial conditions: $\theta_{B,in} = 1.0$, $\theta_{C,in} = 0.0$.

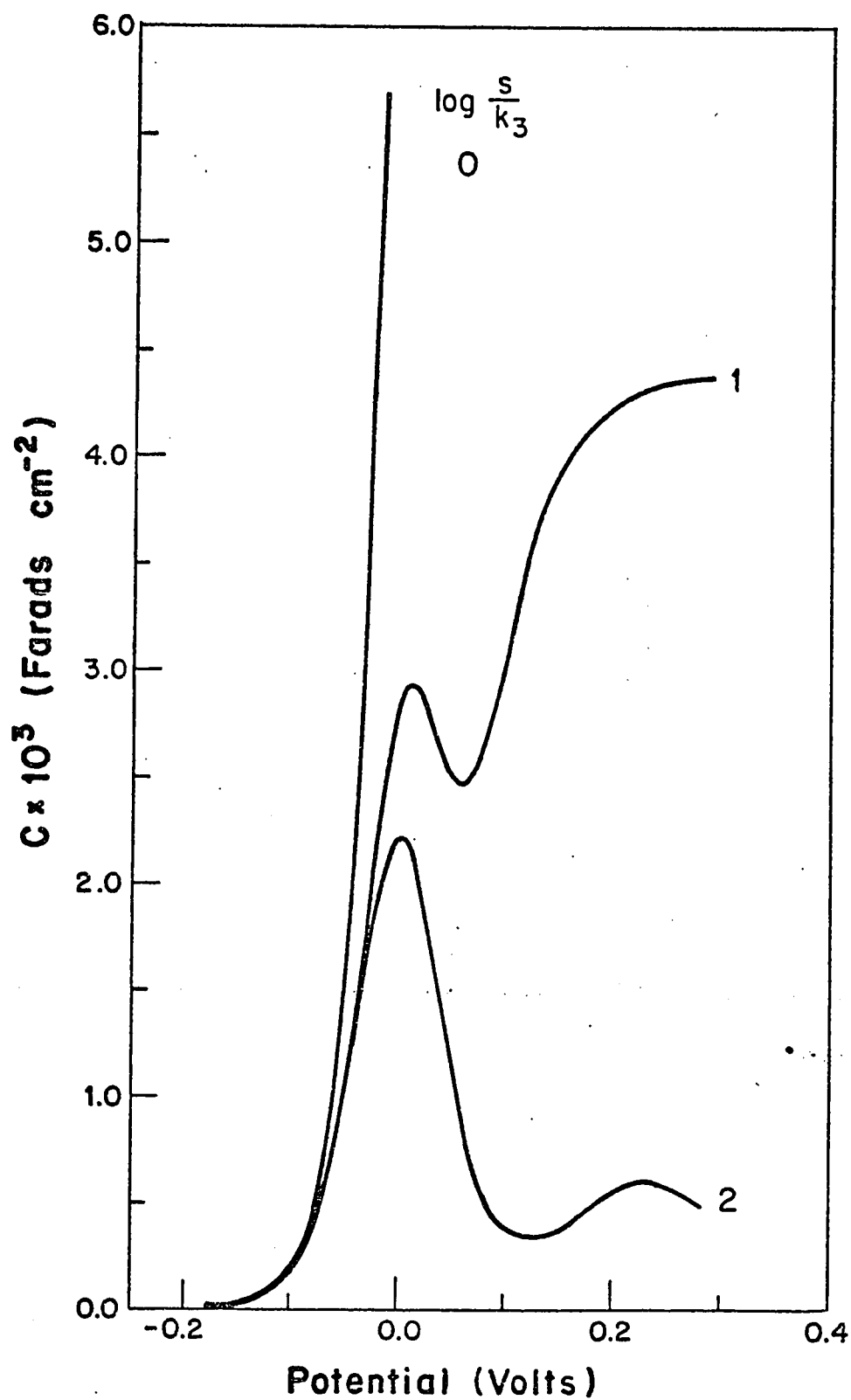


Fig. 7-2 Plots of C vs. V profiles for reaction mechanism (VI)

for various s/k_3 ratios. $E_2^0 = 0.0 \text{ V}$, $E_3^0 = -0.2 \text{ V}$
 $\frac{k_1}{k_3} = 100$.

Initial conditions: $\theta_{B, \text{in}} = 1.0$ and $\theta_{C, \text{in}} = 0.0$

(These C - V profiles were obtained from the curves of Fig. 7-1 by dividing the current by the sweep-rate, s).

increase of the sweep-rate. The final current, however, will never drop below the value of i_{Lim} for step [1].

(ii) The reversible peak for reaction [2] can only be observed (see Fig. 7-1) if the current for the irreversible electrochemical process [3] is much smaller than that for process [2]. This condition is satisfied when the chemical step [1] cannot supply additional amounts of species B and C produced by dissociation of species A at the electrode on the freshly regenerated free surface.

(iii) The peak corresponding to process [3] will start to appear (see Fig. 7-1) only when the s/k_3 ratio is approximately equal to or higher than a given k_1/k_3 ratio. With change in the k_1/k_3 ratio, it is clear that if the current peak for step [3] is still to be resolved, then s/k_3 must also have been changed correspondingly. For values of s/k_3 less than the k_1/k_3 ratio, the current in the potentiodynamic sweep will increase more slowly until the i_{Lim} value is reached. Also it is obvious that there must be a significant difference between the E_2° and E_3° values for steps [2] and [3] if the two peaks are not to completely overlap. With E_3° more and more negative, the peaks can only be separated at relatively high s/k_3 values if process [3] is substantially more irreversible than the other, as assumed here.

For the initial condition (a) the second peak, if observed, will always be much smaller than the one corresponding to the reversible electrochemical reaction [2]. The reason is that the quantity of species C adsorbed during the sweep will depend on time during which the dissociative chemical reaction [1] is allowed to proceed on the freshly regenerated surface, after some of the species B originally adsorbed on the surface is oxidatively desorbed to solution-soluble species D. Hence with increasing sweep-rate, i.e., over shorter times, the amount of C adsorbed on the surface will diminish. If more species C is to be put on the surface it is then necessary to decrease the sweep-rate, i.e., increase the time, but for such a condition no current peak would be observed.

7.4.2 Initial conditions- Case (b)

The second initial condition (b) considered is a more realistic one which would arise at the beginning of a new run, since both species B and C would then be present in equal amounts on the surface. Figs. 7-3 and 7-4 show i - V and C - V curves, respectively, obtained for different s/k_3 ratios. Since all the other parameters are the same as used in Figs. 7-1 and 7-2, direct comparison of the curves is possible.

It can be seen from Figs. 7-1 and 7-3 that there is no difference between curves for $\log \frac{s}{k_3} = 0$ (the two curves are superimposable). For $\log \frac{s}{k_3} = 1$ and 2, differences can, however, already be seen. For $\log \frac{s}{k_3} = 1$ only a shoulder is observed in Fig. 7-3,

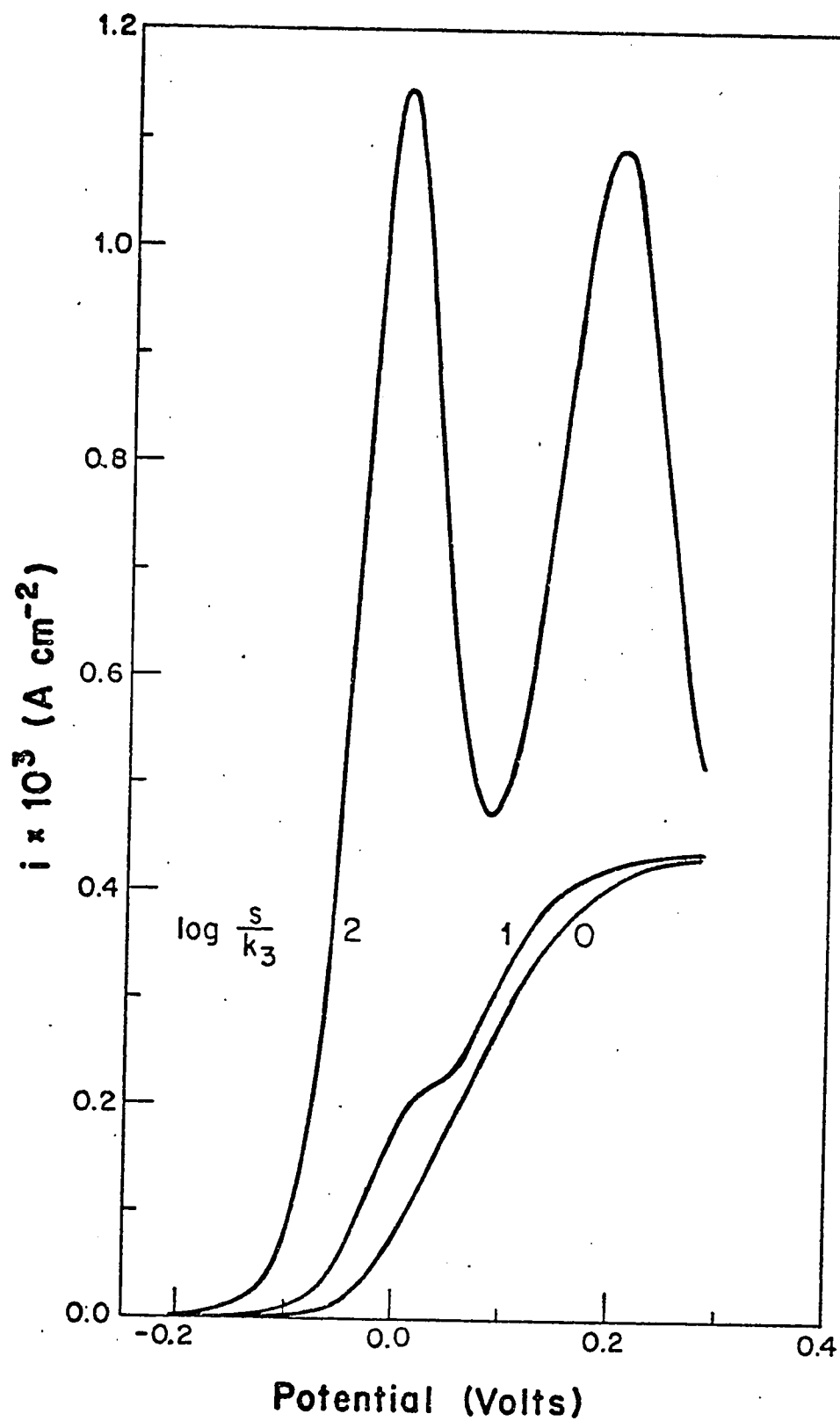


Fig. 7-3 Anodic i - V profiles for reaction mechanism (VI) for various values of s/k_3 and for initial coverages $\theta_{B,in} = \theta_{C,in} = 0.5$. $E_2^\circ = 0.0$ V, $E_3^\circ = -0.2$ V and $\frac{k_1}{k_3} = 100$.

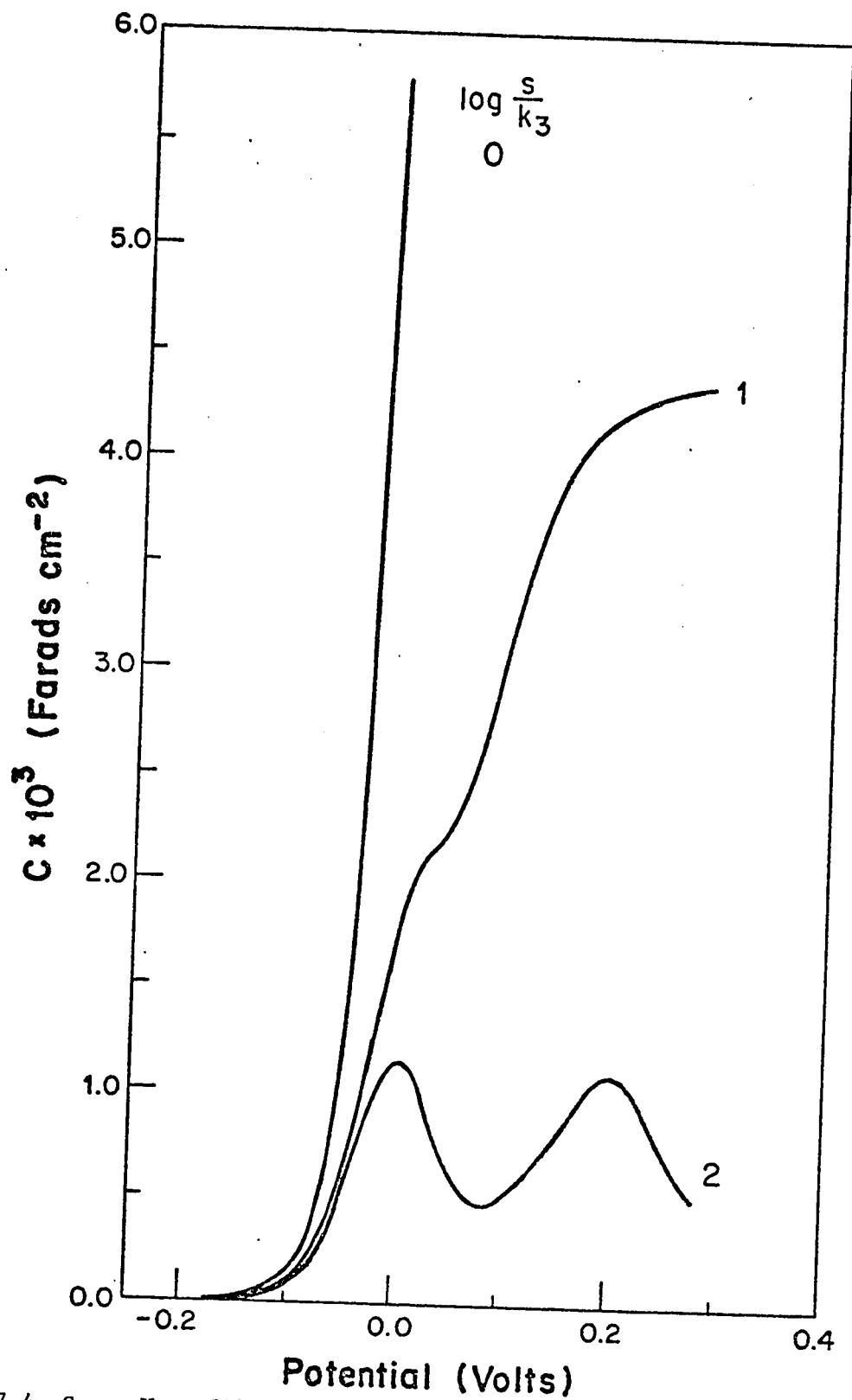


Fig. 7-4 C vs. V profiles for reaction sequence (VI) for various s/k_3 values and for initial coverages $\theta_{B,in} = \theta_{C,in} = 0.5$. $E_2^0 = 0.0$ V, $E_3^0 = -0.2$ V and $\frac{k_1}{k_3} = 100$. (The profiles in this figure were obtained from the i - V curves of Fig. 7-3 by dividing values of i by s).

whereas a small but definite peak is seen in Fig. 7-1. Since the initial coverage of species B is higher in Case (a) than in Case (b) the current and pseudocapacitance, and the corresponding maxima are larger for the former case. A similar explanation applies for the curves for $\log \frac{s}{k_3} = 2$. The maxima corresponding to the reversible electrochemical reaction [2] are about half as high in Figs. 7-3 and 7-4 as those in Figs. 7-1 and 7-2, and conversely the peak for process [3] is relatively more pronounced in the two former figures. The reason is that the sweep is started with half the surface being covered with species C in Case (b), but zero initial coverage of C in Case (a). In the latter case, the second peak arises only on account of dissociative adsorption of species A on the free surface regenerated during the sweep, when species B originally covering the whole surface is being removed, as mentioned before (see Section 7.4.1).

The same explanations concerning the resolution of current and pseudocapacitance peaks for the two parallel electrochemical reactions [2] and [3], discussed for Case (a), apply also to the second set of initial conditions, i.e., Case (b), with only one exception. Whereas in Case (a) the pseudocapacitance peak for reaction [3] decreases continuously with increasing sweep-rate, in the present case the pseudocapacitance peak for process [3] decreases at first, but then remains constant and only shifts to more positive potentials with further increase of the sweep-rate. The reason for decrease of this pseudocapacitance peak is that at higher sweep-rates, i.e., at shorter times, less reactant species A can be dissociatively adsorbed on the

free surface to produce species C, which is then oxidized; therefore, the oxidation peak for C decreases. However, in Case (b), half the surface is already covered by species C at the beginning of the sweep and the pseudocapacitance peak corresponding to this original amount therefore remains constant at sufficiently high sweep-rates. Further increase in the sweep-rate can then make no more change in the height of this peak.

This effect, as explained above, is exemplified in Fig. 7-5, where a change of sweep-rate affects the height of the oxidation peak for species C. It can be observed that only a quite small change ($\leq$ one decade) is required since, at higher sweep-rates, the two peaks will be so far apart that the two electrochemical reactions can then be studied separately, i.e., as two independent electrochemical surface reactions. At sweep-rates slightly lower than the one corresponding to $\log \frac{s}{k_3} = 1.477$ (see Fig. 7-5), the peak for the irreversible electrochemical process [3] will not develop and only the limiting current, i_{Lim} , will eventually be reached.

The changes in θ_B , θ_C and θ_{Tot} as a function of potential for various values of $\log \frac{s}{k_3}$ are shown in Fig. 7-6. The curve for θ_B , taking $\log \frac{s}{k_3} = 2$, approaches the curve for Langmuir adsorption for a species having the maximum available coverage 0.5 (because C occupies the other half of the surface in this case). As the sweep-rate decreases, however, the curve ceases to resemble that for Langmuir adsorption behaviour. An increase in θ_B is observed at the beginning of the sweep and is the result of the tendency for the reversible

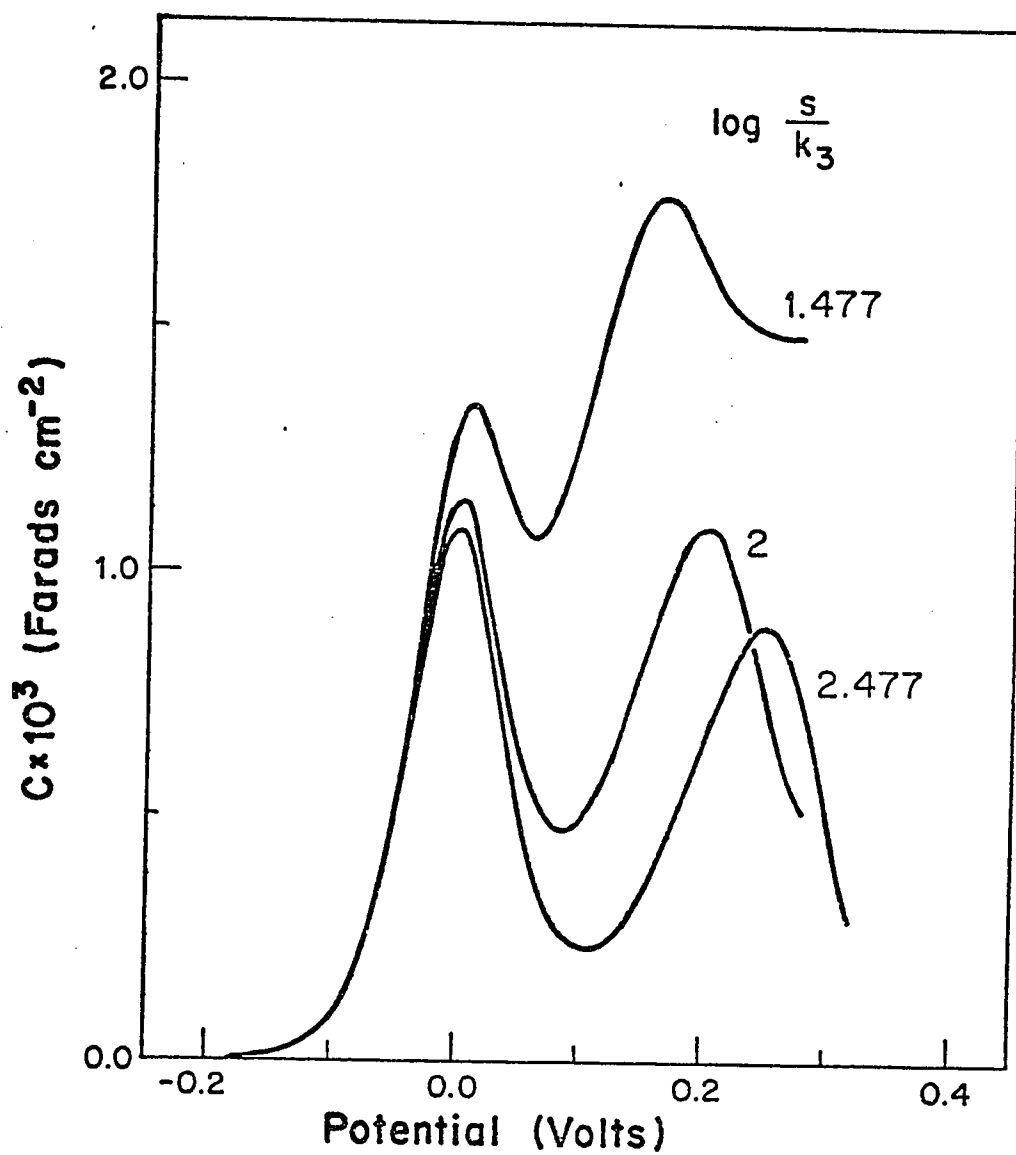


Fig. 7-5 Plots of C-V profiles for reaction mechanism (VI) for values of s/k_3 exemplifying the appearance and gradual shift of the second peak. Initial coverages of species B and C are $\theta_{B,in} = \theta_{C,in} = 0.5$. $E_2^0 = 0.0$ V, $E_3^0 = -0.2$ V and $k_1/k_3 = 100$.

electrochemical reaction [2] to establish equilibrium coverage at each potential, when small enough sweep-rates are used (i.e., $\log \frac{s}{k_3} = 0$ and 1). The reason for this effect is the following: Since θ_C decreases during the sweep, thus regenerating free surface, solution-soluble species D as well as species A can react with free metal surface sites to form more B species. The lower the sweep-rate used, the higher would become the maximum in θ_B until, limitingly, adsorption behaviour for species B having maximum coverage $\theta_B = 1.0$ would be observed.

Increase in θ_C , when $\log \frac{s}{k_3} = 0$, after the initial decrease (see curve for θ_C in Fig. 7-6) during the sweep arises because of the tendency for reaction [2] to maintain equilibrium coverage of B and thus influence process [3] as well. Of course, it also means that the rate of dissociative adsorption of species A is higher than the rate of removal of the adsorbed species C from the surface in this particular potential region but not as high as the rate of step [2] (see Fig. 7-6, θ_C curve for $\log \frac{s}{k_3} = 0$). If the value of $\log \frac{s}{k_3}$ were even lower, the minimum in θ_C versus V in Fig. 7-6 would be more pronounced. For $\log \frac{s}{k_3} > 0$, the θ_C curve shows a continuous decrease, which is consistent with the predictions that dissociative chemisorption becomes rate-determining at higher sweep-rates and hence no further adsorption of species A occurs during the sweep.

The relations for θ_{Tot} do not show any characteristic features except that the profiles become less smooth and may show a shoulder or a plateau at $\theta_{Tot} = 0.5$, depending on the log of the ratio s/k_3 .

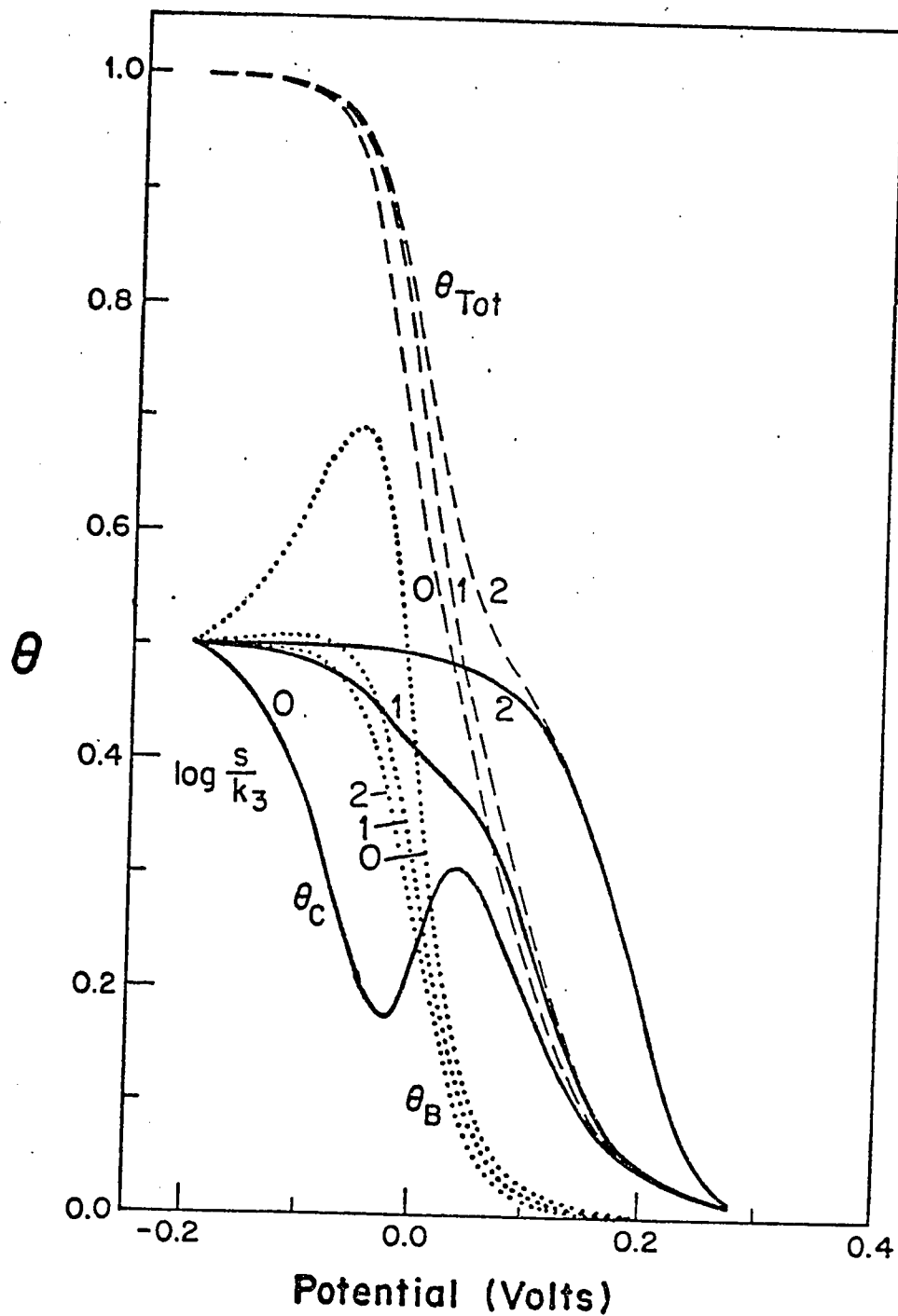


Fig. 7-6 Adsorption behaviour of species B and C as a function of potential V for reaction mechanism (VI) for various s/k_3 ratios. Both θ_B and θ_C as well as θ_{Tot} are plotted. Initial coverages of θ_B and θ_C are 0.5 and $E_2^0 = 0.0$ V, $E_3^0 = -0.2$ V, $\frac{k_1}{k_3} = 100$.

7.5 Summary of Characteristic Features of C-V and i-V Profiles for Reaction Mechanism (VI)

From the C-V and i-V profiles (Figs. 7-1, 7-2, 7-3, 7-4 and 7-5), a number of characteristic features of the kinetic behaviour of this reaction mechanism (VI) can be derived and compared with those of sequence (IV) treated in Chapter VI. By changing the sweep-rate, a series of characteristic profiles is observed. First, two peaks can appear for this reaction sequence (VI), compared with only one in sequence (IV). The height of the peak corresponding to the irreversible electrochemical reaction [3] depends on the initial coverage θ_C , as well as on the sweep-rate and the rate constant for the dissociative chemical reaction [1]. For sequence (VI), the value of i_{Lim} is twice as large as for sequence (IV), assuming the same value of the rate constant k'_1 in both reaction mechanisms, provided that the charge, Q , for a monolayer is known. From the limiting current, the value of the chemical rate constant of step [1] in reaction mechanism (VI) can be determined in the usual way using the equation

$$i_{Lim} = 2Qk'_1 c_A \quad (7-8)$$

The values of the rate constants $k_2 = k'_{-2}$ of the reversible electrochemical reaction [2] cannot, however, be determined because this reaction is assumed to be at equilibrium for all the sweep-rates that can, in practice, be used. However, the value of E_2° may easily be determined from an i-V or C-V curve where the two peaks are reasonably well separated.

If the value of E_3° could somehow be known or could be determined, then it would be possible to derive the value of the rate constant k_3 for the irreversible electrochemical reaction [3], provided that the initial coverage of species C is not zero. This is a necessary requirement, since the rate constant k_3 can only be determined from the sweep-rate dependence of V_p ; however, this is only possible when the two peaks, corresponding to the two electrochemical reactions [2] and [3], are well separated. Otherwise the peak potential is affected by the reversible electrochemical process [2] so that a slight shift in V_p may result. In reality, however, E_3° cannot be determined and thus even the value of k_3 may not be evaluated, but it is possible to determine the product $k_3 \cdot \exp(-\frac{E_3^\circ}{b})$ from a plot of V_p versus $\log s$.

CHAPTER VIII

KINETIC LAWS GOVERNING SURFACE OXIDATION OF NOBLE METAL ELECTRODES

8.1 Introduction

The theory of formation of oxide films tens or hundreds of monolayers thick was developed fully by Mott¹⁴⁷ and his School. Recently, reviews of oxidation of metals and of place-exchange mechanisms in thin layers have appeared and experimental laws governing these processes have been discussed^{148,149}. It is generally found that the extent of growth of the film at constant potential is logarithmic in time^{104,105,126,150}. For thick film growth of the kind treated by Mott it has been shown that the electric field across the growing film causes oxidation of the metal by formation and injection of cations into the film followed by their field-assisted activated migration through the film.

More recently, similar logarithmic laws of extension of oxide films have been observed at Pt^{104,105,126} and other noble metals where less than a monolayer of oxide exists initially. For such conditions it is difficult to see how a Mott high-field growth type of mechanism could be applicable, although it has been invoked in papers by Ord and Ho¹⁵¹ and by Damjanović et al^{152,153}. Hence a problem exists concerning how a logarithmic law can arise for the extension of films below or near a monolayer in extent.

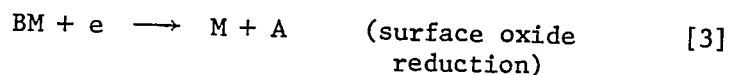
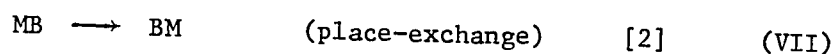
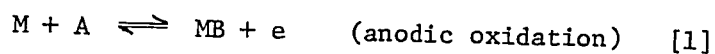
In the initial stages of oxidation of noble metal surfaces a number of important characteristic features can be observed. When oxygen species such as OH or O are deposited on the electrode surface up to a monolayer during a linear potentiodynamic sweep, several distinguishable states of adsorption can be seen⁶⁶. Experimentally, more extensive oxidation of the surface can be generated in two ways:

(a) the potential can be increased to more positive values, i.e., beyond that corresponding to ca. 1-e per metal atom, which would produce a monolayer of OH or (b) a constant potential, which corresponds initially to formation of an oxide film below monolayer coverage, is maintained for a certain time.

If the sweep is reversed after establishing some extent of surface oxidation so that the surface oxide is reduced, an interesting feature is observed: the cathodic i-V profile is completely different from that generated in the anodic-going sweep⁶⁶ except at very low coverages. This effect is attributed to the hysteresis¹⁰⁴ arising in anodic formation and cathodic reduction of the oxide and involves a totally irreversible phase transition in the ad-layer. This transition is referred to as a place-exchange process⁶⁵. It occurs between metal atoms and electrodeposited OH and/or O species on the surface by a quasi-two-dimensional interchange process. It is this place-exchange process which must be considered as a mechanism of extension of sub-monolayers of oxide on metals and also probably for the very early stages of multilayer growth.

8.2 Formulation of a Reaction Mechanism which Includes a Place-Exchange Process

The place-exchange process has an interesting relation to some of the other complex electrode sequences treated in previous chapters. The simplest reaction mechanism which can be formulated is a special example of the "ec" type of mechanism discussed in Chapter VI [see reaction sequence (V)]. However, as will be shown later, the "chemical" step for the oxidation process should be zero-order rather than first-order [see Chapter VI, reaction mechanism (V)]. The place-exchange reaction is, however, usually irreversible as indicated by the hysteresis observed so that reduction must occur via a different reaction pathway in order to recover the initial free surface of the metal. The simplest reaction mechanism involving a place-exchange process consists, therefore, of three steps as follows:



where B is an electrodeposited oxygen species, OH or O, and A is H₂O or OH⁻. Experimental results indicate that step [1] can be assumed to be at equilibrium up to quite large sweep-rates. Step [2], representing the place-exchange reaction, is considered to be totally irreversible and should lead to the direct logarithmic rate law (see Part 8.3). Reaction [3], which regenerates free metal surface sites

M (and reactant A), is also assumed to behave irreversibly in accord with experimental indications for Pt and Au⁶⁴.

The effect of the place-exchange process [2] on the behaviour of the reversible reaction [1] at a constant potential V is that it is made possible for more species B to be deposited on the uncovered portion of the free metal surface M below the potential which would otherwise be required for such a coverage to be generated at equilibrium according to the isotherm for species B alone [e.g., see Chapter I, p.19, eqn. (1-5)] had process [2] not been occurring. Hence, on account of the time-dependent place-exchange process, it is possible to continue to electrodeposit species B at a constant potential, until the rate of the place-exchange process at that potential becomes negligible. It is this combination of reactions [1] and [2] which may generate a logarithmic law in time for extension of the oxide film at a given potential.

When the kinetic behaviour of reaction mechanism (VII) was numerically evaluated, it was not possible to simulate the type of results obtained experimentally^{104,105,126,150} where the charge q for metal surface oxidation increases linearly with log t during the holding time, t, at a constant potential. It should be pointed out that q is a measure of the quantity (below a monolayer this would be proportional to the coverage) of surface oxide species formed as a function of time t. While experimentally the logarithmic relation holds over many decades of time, the simulated behaviour gave a log t relation only over one decade of t or less. Several modifications of

reaction mechanism (VII) were considered, e.g., including another reversible reaction prior to the place-exchange step, but no significant improvements resulted in the simulation of the logarithmic law for longer times. It seems that a possible reason for not obtaining an extended logarithmic relationship could be that it was assumed that the extent of surface oxidation was limited to 1-e per metal atom. As is well known experimentally, higher degrees of oxidation corresponding, e.g., to 2 or 3 electrons per metal atom can be observed.

Since reaction mechanism (VII) does not account for the experimentally observed surface oxidation behaviour^{104,105,126,150}, the problem of the kinetics of the oxidation of surfaces of noble metal electrodes was approached in a different way. While for the other reaction mechanisms dealt with in this thesis, the approach was to assume a reaction mechanism and then seek the kinetic behaviour which would arise under various "experimental" conditions, in this chapter an opposite procedure was adopted. Knowing the experimentally characterized kinetic behaviour of surface oxidation processes, forms of rate laws which might account for the observed behaviour will be discussed and appropriate mathematical equations will be considered (see Part 8.3, below).

8.3 The Logarithmic Rate Law in Oxidation Processes

The question of how a logarithmic growth law for surface oxidation could arise has been considered not only in the electrochemical literature^{104,105,126,150} but also in that concerned with metal

oxidation from the gas phase^{65,154,155}. Experimental data usually fit either a direct logarithmic growth relation, i.e., $q \sim \log t$, and an inverse one $\frac{1}{q} \sim -\log t$ equally well. However, from the mathematical point of view, a better basis for a direct logarithmic law than for an inverse one can be given, as will be discussed below.

Some attention has been paid to the mathematical formulation of both direct^{156,157} and inverse¹⁵⁸ logarithmic growth laws in the past. However, it can be shown that while a direct logarithmic relation can lead to an exact rate law on differentiation, this is not so for the equation representing inverse logarithmic growth behaviour. Conversely, if an approximation is made for the rate equation which can be derived by differentiation of the inverse logarithmic law, then on back integration of that equation only by an approximation can the inverse logarithmic growth equation be recovered. This problem does not arise when both the rate and the corresponding integrated equation for the direct logarithmic law are considered. This seems to indicate that the direct, rather than the inverse, logarithmic law may represent the experimental behaviour better. It is for the above reasons that further attention will be focussed only on the direct logarithmic growth law and the rate equation from which it originates.

8.4 Effects of Changing the Parameters in the Direct Logarithmic Rate Law Equation and Possible Relations for these Parameters

Mathematically, it is easily seen that a rate law which on integration yields a direct logarithmic growth law^{*} must have the

^{*}Since, from now on, only the direct logarithmic relation will be considered, the word "direct" will be omitted in the text which follows.

following form:

$$\frac{dq}{dt} = k \exp(-Lq) \quad (8-1)$$

where k and L are given constants. Integrating eqn. (8-1) yields the following logarithmic relation.

$$q = \frac{1}{L} \ln [kLt + \exp(Lq_{in})] \quad (8-2)$$

where q_{in} is the value of q at $t = 0$. It is to be noted that the rate law given by eqn. (8-1) is, and has to be, "zero-order" in q (or coverage) in the pre-exponential term otherwise such an equation will not give the required linear logarithmic relation in time such as that in eqn. (8-2).

Rearranging eqn. (8-2) gives:

$$q = \frac{1}{L} \ln kL + \frac{1}{L} \ln \left[t + \frac{\exp(Lq_{in})}{kL} \right] \quad (8-3)$$

From eqn. (8-3) it is quite obvious that a relationship of the form $q \sim \ln t$ will only arise if

$$t \gg \frac{\exp(Lq_{in})}{kL} \quad (8-4)$$

When condition (8-4) obtains, eqn. (8-3) can be simplified to

$$q = \frac{1}{L} \ln kL + \frac{1}{L} \ln t \quad (8-5)$$

Eqn. (8-5) represents the logarithmic growth law in its simplest form where the slope is given by $1/L$ and the intercept for $t = 1$ (since a log scale in t is involved) by $\frac{1}{L} \ln kL$ (see Fig. 8-1). Of course,

deviations from linearity must be observed at sufficiently low values of t where the condition (8-4) no longer holds. Normally, however, a corrected time scale would be employed at short times with the integration constant term evaluated empirically.

Defining the slope $1/L$ as σ , i.e.,

$$\sigma = \frac{1}{L} \quad (8-6)$$

gives eqn. (8-3) in the form

$$q = \sigma \ln \frac{k}{\sigma} + \sigma \ln \left[t + \frac{\sigma}{k} \exp\left(-\frac{q_{in}}{\sigma}\right) \right] \quad (8-7)$$

For given σ and k values it is obvious that eqn. (8-7) corresponds to a unique relation between q and $\ln t$. However, experimentally a series of logarithmic growth-law lines can be observed, depending on the holding potential (see Fig. 8-1). Hence either σ or k values, or both, must be potential-dependent. It is useful to consider the three possible cases which can arise and to see how the conditions affect the logarithmic growth law [eqn. (8-7)].

(a) Case (I) - $\sigma = \text{constant}$ and $k = f(V)$

First the case where σ is constant and k depends on the applied holding potential V is considered. From eqn. (8-1) it is obvious that k is the rate constant of the place-exchange process. If this depends exponentially on the field in the usual way for an electrochemical process, then

$$k = k_0 \exp(xV) \quad (8-8)$$

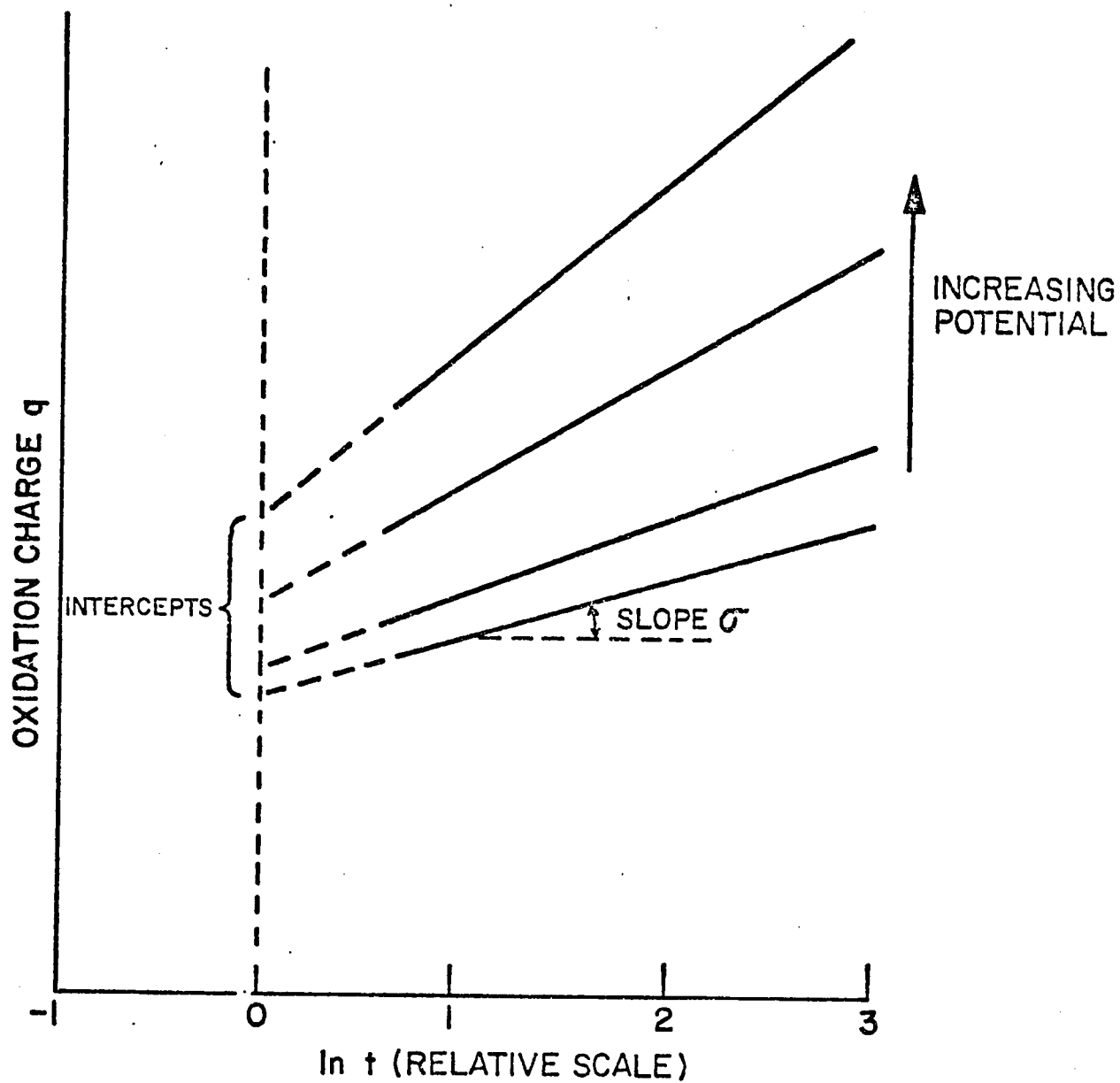


Fig. 8-1 Schematic representation of the plots of oxidation charge q as a function of $\ln t$ for increasing potentials V at which holding for a given time t is performed. Changing slopes σ and intercepts are exemplified. The behaviour shown is typical of that observed experimentally.

where k_o and x are constants independent of the holding potential, and the field at the electrode interface is assumed to be proportional to the interfacial potential difference V . Then substituting eqn. (8-8) into (8-7) gives

$$q = \sigma \ln \frac{k_o}{\sigma} + \sigma x V + \sigma \ln \left[t + \frac{\sigma}{k_o} \exp \left(\frac{q_{in}}{\sigma} - xV \right) \right] \quad (8-9)$$

If

$$t \gg \frac{\sigma}{k_o} \exp \left(\frac{q_{in}}{\sigma} - xV \right), \quad (8-10)$$

it is seen that the relation between q and $\ln t$ is a straight line the slope of which is independent of the holding potential. Since it is assumed that the rate of the place-exchange reaction given by eqn. (8-1) increases with increasing potential, the constant x in eqn. (8-8) must be positive. When both σ and x are positive, the intercept at $t = 1$ (see Fig. 8-1) is linearly dependent on V and increases with increasing potential. This is also observed experimentally^{105,126}. It should be also pointed out that condition (8-10) will be satisfied at shorter times as the potential V increases if

$$\frac{q_{in}}{\sigma} < xV \quad (8-11)$$

which seems to be the case if $x = \frac{1}{b} = \frac{\beta F}{RT} \div 20$.

(b) Case (II) - $k = \text{constant}$ and $\sigma = f(V)$

The second case to explore is that where k is constant but the slope σ is linearly dependent on V , i.e.

$$\sigma = yV \quad (8-12)$$

if $\sigma = 0$ when $V = 0$. Here y is a positive constant, independent of potential. The reason for assuming a linear rather than, for example, exponential relation between σ and V is that the $\sigma = \frac{1}{L}$ term appears already in the exponent of the rate equation (8-1). It seems therefore more appropriate to consider a linear relationship given by eqn. (8-12). Then eqn. (8-7) will have the form

$$q = yV \ln \frac{k}{yV} + yV \ln \left[t + \frac{yV}{k} \exp\left(\frac{q_{in}}{yV}\right) \right] \quad (8-13)$$

As mentioned above, the slope will increase linearly with potential when

$$t \gg \frac{yV}{k} \exp\left(\frac{q_{in}}{yV}\right) \quad (8-14)$$

However, the intercept for $t = 1$ when condition (8-14) holds, depends strongly (see Figs. 8-2, 8-3) on the value of the rate constant k . For low values of k , the intercept will decrease with increasing slope σ , i.e., with increasing V for a constant value of y . For high values of k , the intercept will increase with increasing slope at first, but it then reaches a maximum and with further increase of σ the intercept decreases again. A general normalized shape for the relation between the intercept and σ is shown in Fig. 8-2 and is based on dividing both the intercept and the slope by the rate constant k . The effect of various values of the parameter k on the profiles of intercepts plotted against slopes is exemplified in Fig. 8-3. It can be shown that the maximum in the curves arises when $\sigma = k \exp(-1)$ and the intercept has the same numerical value, i.e., $k \exp(-1)$ (see Figs. 8-2 and 8-3).

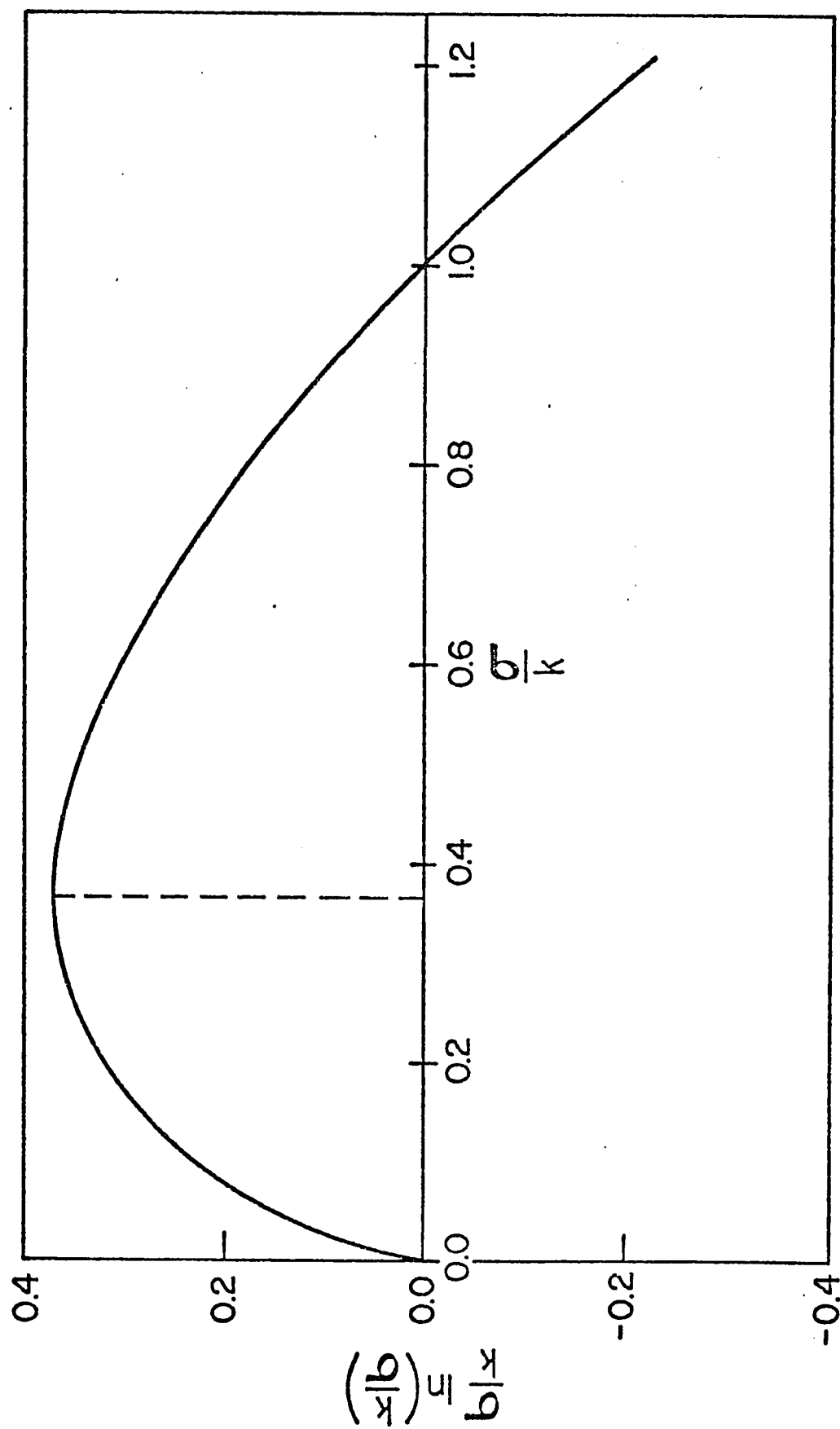


Fig. 8-2 Plot of reduced intercept $\frac{\sigma}{k} \ln \frac{k}{b}$ as a function of reduced slope $\frac{\sigma}{k}$ for Case (II)
(see text, p.159).

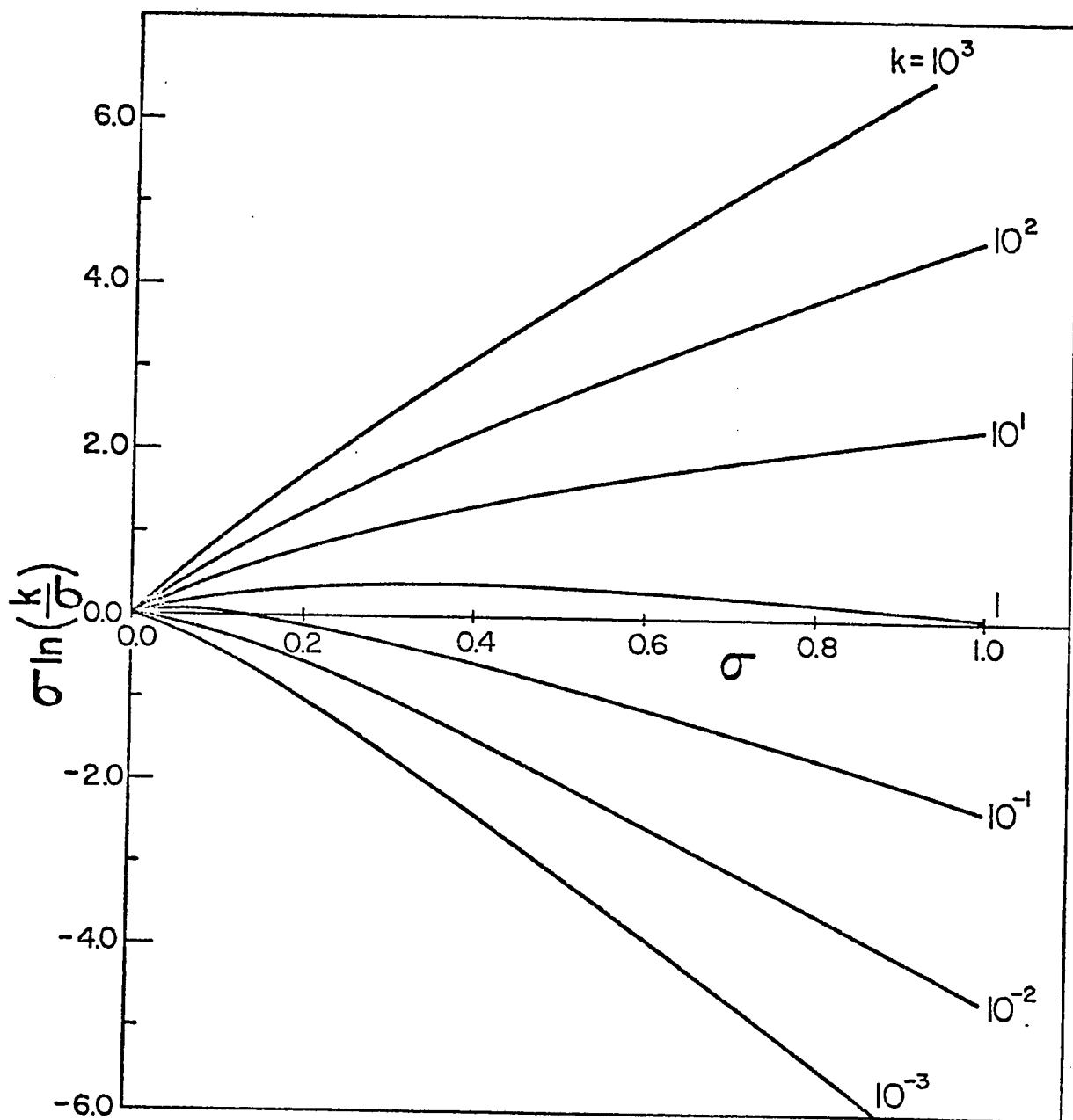


Fig. 8-3 Family of curves of intercepts $\sigma \ln \frac{k}{\sigma}$ plotted vs. slopes σ for various values of the parameter k for Case (II) (see text, p.159).

It should be pointed out that the r.h.s. of condition (8-14) does not always diminish with increasing potential depending on the values of y and q_{in} . The parameters y and q_{in} , together with the magnitude of the value of the rate constant k , will determine the limit in time t below which deviation from a linear q vs. $\ln t$ plot will begin to be significant, i.e., condition (8-14) will not hold.

From the above examination of Case (II), it can be concluded that this case does not conform at all to the behaviour observed experimentally.

(c) Case (III) - $k = f(V)$ and $\sigma = f(V)$

A third and final possibility can arise where both the slope σ and the rate constant k are potential-dependent. The forms of relations for k and σ are given by eqns. (8-8) and (8-12), respectively, which upon substitution into eqn. (8-7) give

$$q = yV \ln \frac{k_o}{yV} + xyV^2 + yV \ln \left[t + \frac{yV}{k_o} \exp \left(\frac{q_{in}}{yV} - xV \right) \right] \quad (8-15)$$

A logarithmic law will result when

$$t \gg \frac{yV}{k_o} \exp \left(\frac{q_{in}}{yV} - xV \right) \quad (8-16)$$

This is especially true if either x or y are large, as they both appear in the exponent. However, since y also appears in the linear part of the condition (8-16), it is quite obvious that when x is large enough, regardless of the value of parameter y , the above condition will hold. Also, when x is large, the time limit, within which

deviations from the logarithmic law are significant, decreases as the potential increases [cf. eqns. (8-10) and (8-11)].

Once again in this case the slopes of q vs. $\ln t$ relationships will depend on the potential and will increase linearly with increasing V because of the assumed potential-dependence of σ . The function, which determines the behaviour of the intercept of eqn. (8-15) for $t = 1$ when condition (8-16) holds, is quite complicated and will be investigated more closely.

The intercept of eqn. (8-15) is equal to:

$$I = yV \ln \frac{k_o}{yV} + xyV^2 \quad (8-17)$$

The change of intercept with varying potential V is obtained by taking the first derivative of eqn. (8-17):

$$\frac{dI}{dV} = y (2xV - \ln V) + y \ln \frac{k_o}{y} - y \quad (8-18)$$

Hence $\frac{dI}{dV}$ will increase with potential and will be linear in V if

$$2xV \gg \ln V \quad (8-19)$$

and x is reasonably large. If it is assumed that $x = \frac{\beta F}{RT} \doteq 20$ (cf. p.159) then condition (8-19) will always be satisfied and eqn. (8-18) can be approximated by

$$\frac{dI}{dV} = 2xyV + y \ln \frac{k_o}{y} - y \quad (8-20)$$

It is now quite obvious that the intercept, I , will increase parabolically with increasing potential V , which does not seem to be

observed experimentally^{105,126}. However, further experimental studies are required to confirm or refute that conclusion.

8.5 Summary of Conclusions Regarding the Direct Logarithmic Growth Law

It can be concluded that the direct logarithmic law can describe the experimental behaviour of surface oxidation processes occurring by the place-exchange mechanism quite well under certain conditions, i.e., for Cases (I) and (III). Case (II), however, is not consistent with the experimental behaviour. Also, it seems improbable that the rate constant, k , in eqn. (8-1) would remain unchanged with varying potential V , as assumed in Case (II). It is more probable that k will increase with V thus increasing the rate of the place-exchange process [2] described by eqn. (8-1) as appears to occur experimentally.

It is of interest to note that a direct logarithmic growth law can only originate if there is a rate process which is statistically independent of coverage, i.e., zero-order, but which has an activation energy which increases as more and more oxygen species are place-exchanged. Such a process would have to be one where, for example, a metal atom in the surface was injected on to the surface amongst OH and/or O species which then rearrange with an activation energy dependent on coverage and extent of rearrangement.

CHAPTER IX

INHIBITION OF A FARADAIC REACTION BY A SIMPLE 1-e ELECTROCHEMICAL SURFACE REACTION WHICH OCCURS IN PARALLEL

9.1 Introduction

Many anodic reactions, including metal dissolution and organic oxidations, may exhibit inhibition or passivation effects. These passivation effects can also arise in some other reactions, e.g., hydrogen ionization¹⁵⁹.

The passivation behaviour can be observed in steady-state point-by-point current-potential relations but many organic oxidation reactions where effects of this kind occur have been studied by the potentiodynamic method. Complex behaviour can then arise because of (a) time, i.e. sweep-rate dependence of surface coverage of the electrode by the inhibiting species at a given potential and (b) current contributions arising at high sweep-rates from the electrochemical deposition or desorption of the inhibiting species itself. Co-adsorption effects involving two or more chemisorbed species may further complicate the electrochemical behaviour. An analysis of this case is therefore very important as many practically useful oxidation reactions are prevented from developing appreciable current densities by passivating effects that arise from inhibiting species generated from the water solvent or from a step in the main reaction sequence itself or some side reaction sequence, e.g., as in the case of oxidation of HCOOH at Pt^{70,71} (see also pp.447 and 457 of ref. 72).

Passivation effects may arise in two distinguishable ways:

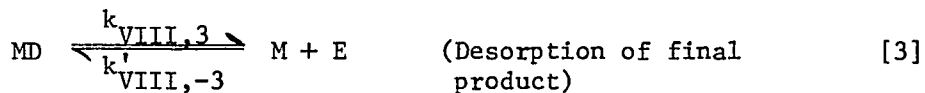
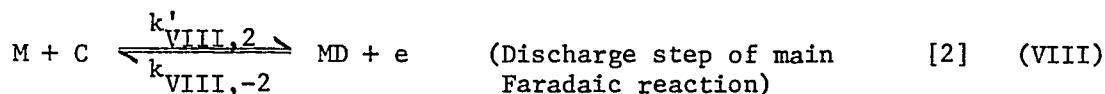
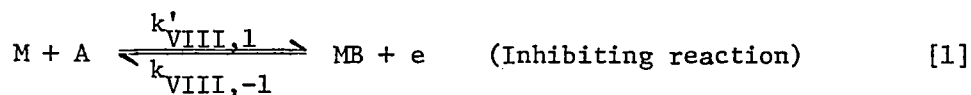
- (i) The first is due to inhibition resulting from modification of the free surface available for the overall electrochemical reaction. The change of the free surface results from an inhibiting species being deposited on the surface in a competing reaction.
- (ii) The second effect is one which arises in certain decompositions of adsorbed species where the products of a surface reaction require two or more adsorption sites for each on which the reacting species was initially adsorbed. This kind of effect will be referred to as self-inhibition.

The kinetic theory of inhibition reactions for both types of cases, when the inhibiting reaction occurs reversibly and follows either Langmuir or Temkin adsorption behaviour was treated in some detail by Gilroy and Conway¹⁶⁰ but not for reactions under potential-dynamic control.

In the present chapter, the significance of Faradaic current peaks in current-potential profiles generated by the linear voltage sweep method will be examined and it will be shown how the peaks can arise kinetically from inhibition effects when the inhibiting reaction behaves either reversibly or irreversibly, depending on the reduced sweep-rate, s/k , i.e., the s employed in the experiment.

An anodic reaction will be considered which is inhibited by the appearance of another species competing for sites on the surface

of the electrode. If the inhibiting species is generated by an electrochemical reaction on the electrode its coverage will vary with the applied potential. In the simulation of the kinetics of an inhibited reaction, a simple 1-e electrochemical reaction of the kind discussed in detail in Chapter IV, is considered to be the "parallel" inhibiting reaction (step [1] below). The overall Faradaic reaction is assumed to take place in two steps, the first of which is the electrochemical process producing an adsorbed intermediate in that Faradaic reaction, which is then desorbed from the surface in a very fast following chemical reaction. For this chemical step, it is assumed that the forward rate constant is much larger than the backward one, so that the reaction can be assumed to behave irreversibly. These two reactions are represented by steps [2] and [3], respectively (see below). Hence the overall reaction mechanism can be represented as follows:



MB and MD represent adsorbed electroactive species at coverages θ_B and θ_D , respectively. MB is the inhibiting adsorbed molecule while MD is the adsorbed intermediate in the main overall

Faradaic process. Species A, C and E^{*} are solution-soluble. As for previous reaction mechanisms investigated, it is assumed that no diffusion limitations arise for any of the above species.

It would also be possible to consider a simpler case where reaction [2] was of the form $M + C \rightarrow D + e + M$ with D being a solution-soluble final product, so that step [3] is absent. Depending on conditions for the sequence [1], [2], [3], this case can give the same results as those deduced below for the more general three-step mechanism.

9.2 Calculation Procedure and Values of Parameters

For details about the simulation technique and numerical methods used, reference is made, as for previous reaction mechanisms considered, to Chapter III and Appendix I.

As in all the other reaction mechanisms treated in this thesis, double-layer effects are assumed to be invariant and are therefore not included in the equations to be derived in Part 9.3, except implicitly in the rate constant values, k.

In the calculations, the solution concentrations c_A , c_C and c_E of soluble species A, C and E, respectively, were as usual taken as 1 mol l^{-1} . Both chemisorbed species B and D were assumed to follow Langmuir isotherms although similar calculations could be carried out for cases where interaction effects ($g \neq 0$) are significant. This

* For explanation see footnote appearing on p.139.

may be true especially of the inhibiting species B in reaction [1] as compared to species D which is maintained at its equilibrium coverage at all times through step [3]. The charge for generating a monolayer by either species B or D was taken as $220 \mu\text{C cm}^{-2}$ for convenience, but for a real system this assumption may or may not apply. The choice of a different appropriate value for one of the two electrochemical steps is always easy. The symmetry factor, β , was again taken as 0.5.

The standard electrode potential for the inhibiting reaction [1], E_1^0 , was chosen to be 0.2 V for computational convenience while that for the Faradaic process, E_2^0 , was taken to be 0.0 V. In order to maintain the coverage of species D very small (e.g., $\theta_D = 10^{-6}$) it is necessary to have the forward rate constant for the chemical step $k_{\text{VIII},3} \gg k'_{\text{VIII},-3}$ (e.g., $\frac{k_{\text{VIII},3}}{k'_{\text{VIII},-3}} = 10^6$). If it is desired to keep θ_D at a constant equilibrium value during the sweep experiment in the potential region of interest, then the backward rate constant of the chemical step [3] must still be greater than the forward rate constant for the electrochemical step [2] modified by the applied potential, i.e., $k'_{\text{VIII},-3} \gg k'_{\text{VIII},2} \exp\left(\frac{\Delta V_2}{b}\right)$.

9.3 Formulation of Kinetic Equations

The total current density, i_{Tot} , observed in a potential sweep experiment is the sum of i_1 , the current density for reaction [1], and i_2 , that for reaction [2]; hence

$$i_{\text{Tot}} = i_1 + i_2 \quad (9-1)$$

The currents for the individual electrochemical processes may be written in the usual way as

$$i_1 = Q \frac{d\theta_B}{dt} = Q [k'_{VIII,1} c_A (1-\theta_B-\theta_D) \exp\left(\frac{\Delta V_1}{b}\right) - k_{VIII,-1} \theta_B \exp\left(-\frac{\Delta V_1}{b}\right)] \quad (9-2)$$

and

$$i_2 = Q [k'_{VIII,2} c_C (1-\theta_B-\theta_D) \exp\left(\frac{\Delta V_2}{b}\right) - k_{VIII,-2} \theta_D \exp\left(-\frac{\Delta V_2}{b}\right)] \quad (9-3)$$

The overall rate of change of θ_D with time is

$$\begin{aligned} \frac{d\theta_D}{dt} = & k'_{VIII,2} c_C (1-\theta_B-\theta_D) \exp\left(\frac{\Delta V_2}{b}\right) - k_{VIII,-2} \theta_D \exp\left(-\frac{\Delta V_2}{b}\right) \\ & - k_{VIII,3} \theta_D + k'_{VIII,-3} c_E (1-\theta_B-\theta_D) \end{aligned} \quad (9-4)$$

Integrating eqn. (9-4) together with eqn. (9-2) yields the coverages θ_B and θ_D at any given time t .

The forward and backward rate constants for reaction [1] were taken to be equal, i.e., $k'_{VIII,1} = k_{VIII,-1}$. In order to have $i_2 = 0$ at the standard electrode potential E_2^0 , which is also the reversible potential $E_{r,2}$ for the Faradaic process since the concentrations of the solution-soluble species are taken as 1 mol l^{-1} (see Part 9.2), then $k'_{VIII,2} = k_{VIII,-2} \theta_D$. Since $k_{VIII,3} \gg k'_{VIII,-3}$ and the rate of the chemical step [3] is taken to be much faster than that of the electrochemical step [2], it is evident that reaction [2] is the rate-determining step in the overall Faradaic process [2], [3].

The modulating potential, ΔV , for the anodic-going sweep is given by (cf., e.g., Chapter IV, Part 4.3, p.93)

$$\Delta V = V - E^\circ = V_{in} + st - E^\circ \quad (9-5)$$

where ΔV_1 is referred to the standard electrode potential E_1° for the surface process [1] and similarly ΔV_2 is referred to E_2° for the electrochemical step [2]. The V_{in} value was chosen as 0.0 V, which corresponds to the standard (and also the reversible) potential taken for the Faradaic process. At the same time, this value of V_{in} is sufficiently negative in comparison with the value of E_1° for the inhibiting surface electrochemical process [1] that the value of $\theta_{B,in}$ can be assumed to be zero or very near zero at that potential. The terms b ($= \frac{2RT}{F}$ for $\beta = 0.5$) and R, T and F have their usual meanings (cf. Chapter IV, Part 4.2, p.93).

9.4 Effect of Sweep-Rate and the Ratio of the Two Electrochemical Rate Constants on the Current-Potential Profiles

When calculations are carried out for reaction scheme (VIII), two types of behaviour can develop, depending on the relative values of the rate constants k_1 and k_2 for steps [1] and [2], respectively. The ratio k_1/k_2 determines the current passed in reaction [1] relative to that for the overall Faradaic reaction step [2] and this depends also on the sweep-rate when process [1] behaves reversibly as will be explained later.

The behaviour for two selected ratios of k_1/k_2 is illustrated in Figs. 9-1 and 9-2, where characteristic i - V profiles, namely the

Tafel plots of V vs. $\log i_{\text{Tot}}$, are plotted for a series of sweep-rate values ranging from reversible to irreversible behaviour of the inhibiting reaction [1]. The curves obtained show the effect of passivation due to species B on the overall Faradaic process [2], [3]; a maximum current is reached after a linear Tafel region and with further increase of potential, the current starts to diminish. The shape of the passivation curves depends solely on the characteristics of the inhibiting reaction [1].

If step [1] behaves reversibly then the $1-\theta_B$ in eqn. (9-3) is determined by equilibrium or quasi-equilibrium in that step, i.e.,

$$1-\theta_B = \frac{1}{1+K_I \exp\left(\frac{\Delta V_F}{RT}\right)}, \text{ noting that } \theta_D \ll \theta_B. \text{ Under these conditions the}$$

V - $\log i_{\text{Tot}}$ profile is symmetrical about the maximum current attained and after a coverage $\theta_B \div 0.5$ has been generated the Tafel slope for step [2] changes from its normal positive value of 0.118 V limitingly to a negative value of -0.118 V as shown in both Figs. 9-1 and 9-2 for $\log \frac{s}{k_1} = -3$ and -2. However, for higher values of s/k_1 reaction [1] is driven to irreversibility so that $1-\theta_B$ is no longer given by the relation above and the V vs. $\log i_{\text{Tot}}$ profile becomes asymmetrical. A situation then develops of the kind shown in Fig. 9-1 for $\log \frac{s}{k_1} = -1$ and 0 where the inhibited current profile merges into the Tafel line of negative slope which arises when step [1] behaves reversibly (see curve for $\log \frac{s}{k_1} = -3$ in Fig. 9-1). Other curves of Fig. 9-1 for $\log \frac{s}{k_1} > 0$ never merge into the Tafel line of negative slope over the range of $\log i$ shown in this figure. However, they will eventually merge if sufficiently low currents had been evaluated at higher potentials for

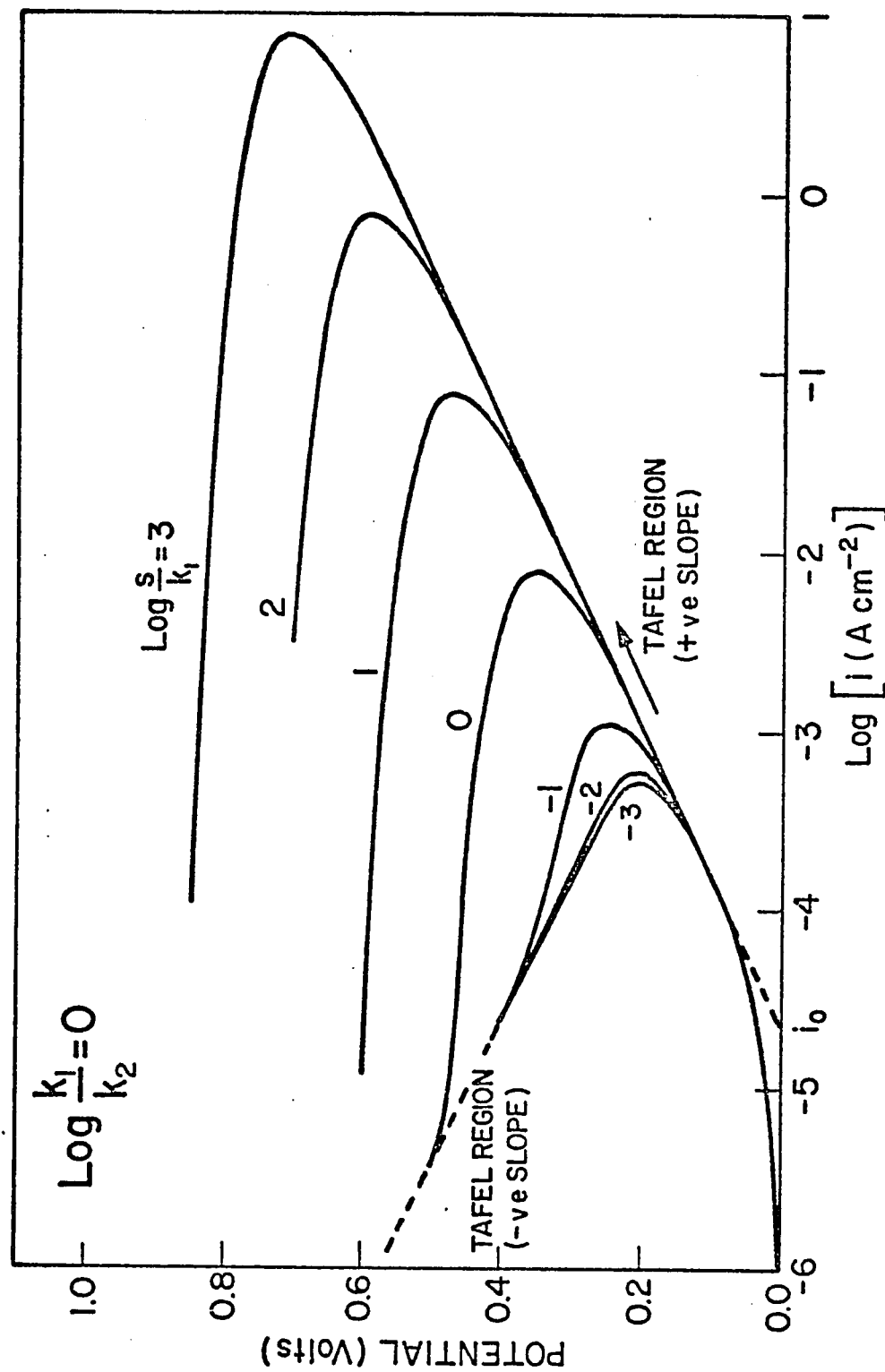


Fig. 9-1 Polarization curves (V vs. $\log i$) for reaction mechanism (VIII) for various values of $\log \frac{s}{k_1}$ and for $\log \frac{k_1}{k_2} = 0$. The exchange current density, i_0 , as well as the positive and negative Tafel slopes are indicated.

the greater $\log \frac{s}{k_1}$ values. It must be mentioned, however, that in general, the negative Tafel slope need not have the same numerical value as the positive Tafel slope. This depends on the reaction mechanism of the inhibiting process, the isotherm for the inhibiting species, the number of electrons required for its production¹⁶⁰ and the value of β .

It can be seen that there is only one common Tafel line in Fig. 9-1, thus giving rise to only one exchange current density, i_0 , whereas several Tafel lines could be generated for conditions referred to in Fig. 9-2 where $\log \frac{k_1}{k_2} = 2$. Also, it is more difficult to obtain the limiting Tafel line with negative slope except at very low $\log \frac{s}{k_1}$ values where the current for the inhibiting reaction [1] attains sufficiently small values not to affect the total reaction current generated by step [2]. The reason for this apparent anomaly lies in the ratio of the two electrochemical rate constants k_1 , for reaction [1], and k_2 , for reaction [2]. For the cases where $\frac{k_1}{k_2} \leq 1$ only one common Tafel line arises independently of the sweep-rate. Under such conditions, the current density, i_1 , for the inhibiting 1-e surface process is always much lower than the current density corresponding to the Faradaic process [2] (Fig. 9-1). However, it must be pointed out that the limiting k_1/k_2 ratio depends on the difference between the standard electrode potentials E_1° and E_2° , which may vary from one system under investigation to another. For conditions where i_1 is comparable with, or greater than i_2 , a different V vs. $\log i_{\text{Tot}}$ profile is obtained when process [1] is reversible (see Fig. 9-2 for $\log \frac{s}{k_1} = -3$ and -2).

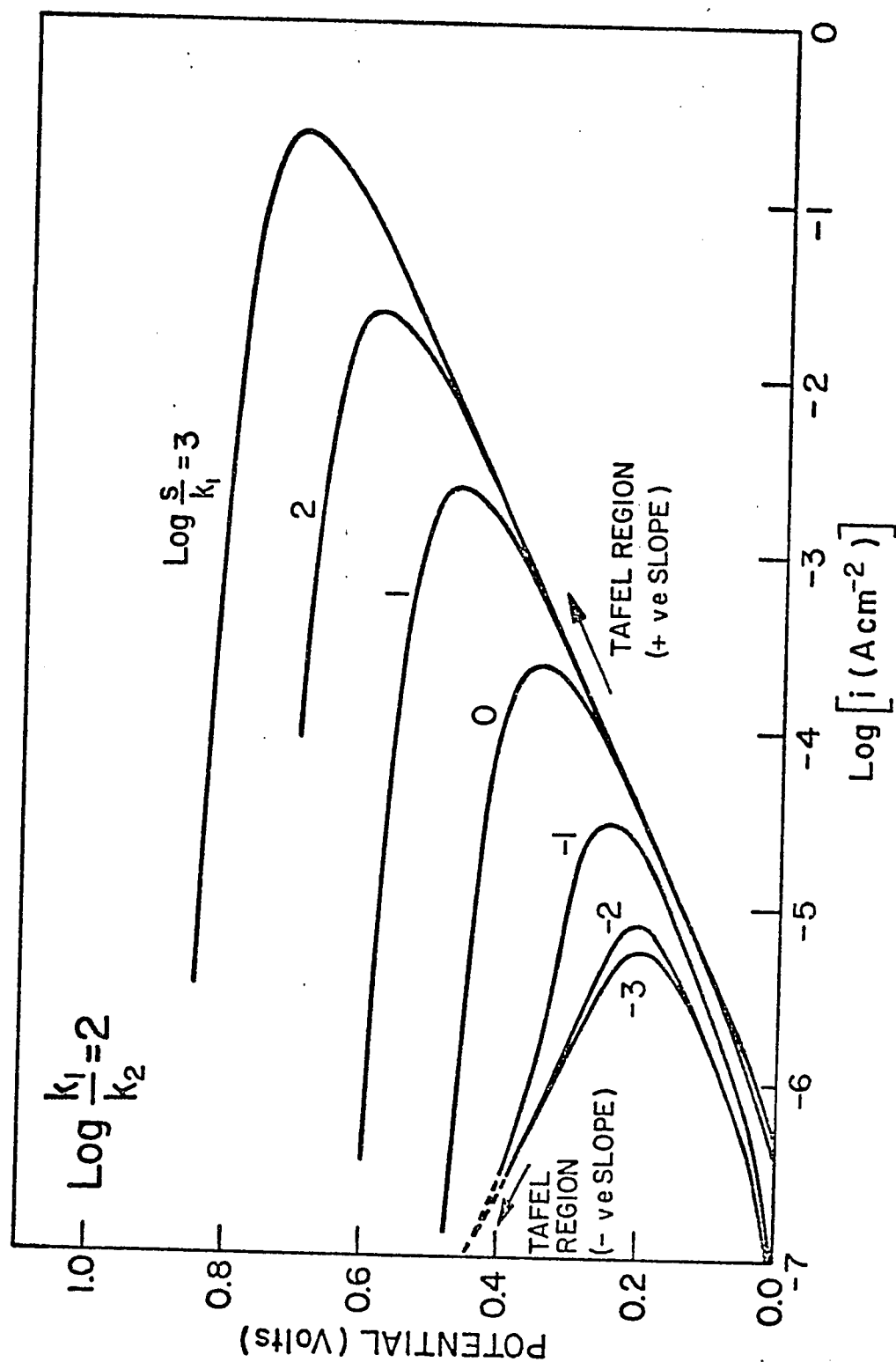


Fig. 9-2 Family of plots of V vs. $\log i$ for reaction sequence (VIII) for various $\log \frac{s}{k_1}$ values and for $\log \frac{k_1}{k_2} = 2$. Tafel regions with both positive and negative slopes are indicated.

This effect may be explained easily. When the simple 1-e electrochemical surface reaction predominates, the currents i_1 and $i_{1,p}$ for both reversible and irreversible conditions increase linearly with s so that the pseudocapacitance values for the two limiting conditions have certain but constant values as shown in Chapter IV. As in the case of reaction [1] under reversible conditions, the values of current and peak current vary but arise at the same potential; also the values of current for process [2] remain unaltered for a given applied potential over the same region. However, an apparent shift of the V vs. $\log i_{Tot}$ curve, i.e., for the total current, on the current scale, as the sweep-rate is varied, is seen. For the case where the inhibiting reaction [1] is irreversible, the effect described above is not observed. The explanation is that with increasing s , e.g., by 10 times, the current peak $i_{1,p}$ also increases 10 times, but at the same time shifts to more positive potentials along the Tafel line.

It can be shown that for any given potential the current density i_1 is a constant fraction of the total current density, i_{Tot} , for a given k_1/k_2 ratio and a given difference between the two standard electrode potentials, under conditions where both reactions [1] and [2] behave irreversibly. The equation representing this situation can be derived and has the following form:

$$i_{Tot} = i_1 \left[1 + \frac{k_2}{k_1} \exp\left(\frac{\Delta E^\circ}{b}\right) \right] \quad (9-6)$$

where

$$\Delta E^\circ = E_1^\circ - E_2^\circ \quad (9-7)$$

Fig. 9-3 shows plots of V vs. $\log \frac{i}{s}$, for process [1] under both reversible and irreversible conditions together with the pseudo-capacitances i_1/s and the reduced total currents i_{Tot}/s for a given k_1/k_2 ratio with ΔE° taken as 0.2 V to illustrate the points discussed above with respect to the behaviour in Figs. 9-1 and 9-2. The main features of the results shown in Fig. 9-3 may be summarized as follows:

- (i) The curve for reaction [1] under reversible conditions remains invariant and hence does not change in shape with varying sweep-rate nor does it shift along the potential scale (Fig. 9-3 for $\log \frac{s}{k_1} = -3$, curve for C_1);
- (ii) The total currents on the reversible curve for the overall reaction mechanism (VIII) can increase or decrease depending on whether the sweep-rate is increased or decreased. This behaviour arises because the overall Faradaic process is independent of the sweep-rate applied (Fig. 9-3 for $\log \frac{s}{k_1} = -3$, curve for i_{Tot}/s);
- (iii) The shape of the curve for reaction [1] when behaving irreversibly does not change, but the whole curve shifts to more positive potentials with (logarithmically) increasing sweep-rate (and vice versa) (Fig. 9-3 for $\log \frac{s}{k_1} = 2$, curve for C_1);
- (iv) The curve for the overall reaction (VIII) behaving irreversibly also does not change its shape. However, in contrast to the case when the overall reaction is reversible [case (ii) above], this curve remains invariant, i.e., reduced currents

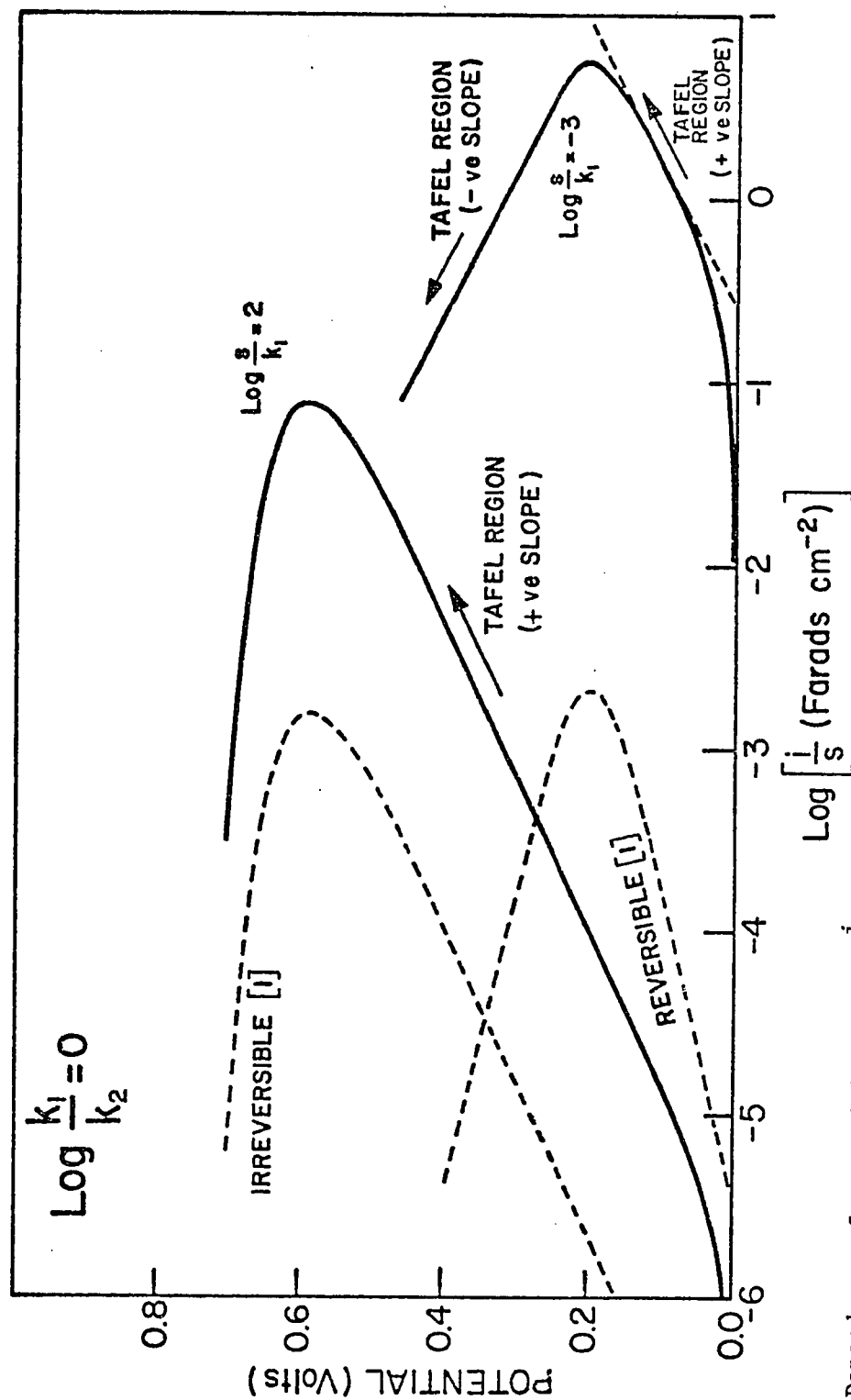


Fig. 9-3 Dependence of potential V on $\log \frac{i}{s}$ is shown for step [1] and overall reaction mechanism (VIII) for cases when process [1] behaves both reversibly ($\log \frac{s}{k_1} = -3$) and irreversibly ($\log \frac{s}{k_1} = 2$). The ratio $\log \frac{k_1}{k_2} = 0$. Tafel regions with both positive and negative slopes are indicated.

on it do not increase or decrease with changing sweep-rate; the whole curve only shifts to more positive potentials with increasing sweep-rate in the same proportions as the irreversible curve for process [1], so that the ratio $\frac{i_{\text{Tot}}/s}{C_1}$ remains constant for a given set of values of k_1 , k_2 and ΔE° . This observation is confirmed by eqn. (9-6), which shows that the ratio of i_{Tot}/i_1 is constant, when both electrochemical processes [1] and [2] behave irreversibly, as discussed earlier.

9.5 Summary of Conclusions on the Behaviour of Reaction Mechanism (VIII) and Procedures for Determination of Kinetic Parameters for the Process

The principal features of this reaction mechanism (VIII) may now be summarized and the bases for determination of the important kinetic parameters given:

- (a) When the inhibiting reaction [1] is in equilibrium, it can be seen immediately how close are the currents i_1 and i_2 , corresponding to the processes [1] and [2], respectively. If the current does not increase or decrease with changing sweep-rate when the inhibiting reaction [1] occurs reversibly, then the current corresponding to reaction [1] is much less than that for reaction [2], i.e., $i_1 \ll i_2$. If the current changes with the sweep-rate, then $i_1 \geq i_2$ and the change is more pronounced the larger is the ratio of the rate constants k_1 and k_2 , where k_1 must be bigger than k_2 . From the

reversible i - V curves, the value of E_1° , the standard electrode potential for the inhibiting reaction, may be obtained;

- (b) If both reversible and irreversible i - V curves can be obtained, then by plotting V_p as a function of $\log s$, the value of s_o can be determined (see Fig. 9-4), (cf. Chapter IV). From the s_o value, the rate constants $k_1' = k_{-1}$ can be calculated using the equation

$$s_o = b k_1 \quad (9-8)$$

- (c) If there is no shift in the current with changing sweep-rate under conditions where process [1] remains reversible, then the rate constant k_2' for the Faradaic reaction [2] can be determined from its exchange current density, $i_{o,2}$ in the usual way. It should be pointed out that for process [2] $k_2' = k_{-2} \theta_D$. This means, therefore, that the value of k_{-2} cannot be determined unless the value of θ_D is known;
- (d) The standard electrode potential, E_2° , for process [2] may be determined provided that $i_1 \ll i_2$. If, however, the value of i_1 is comparable with i_2 (see Fig. 9-2) then the value of E_2° can only be determined from the curve when the inhibiting reaction [1] behaves reversibly. Then by lowering the sweep-rate to a value sufficiently small that eventually the condition $i_1 \ll i_2$ will be reached, determination of E_2° is possible;
- (e) If the current shifts (see lower left-hand region of

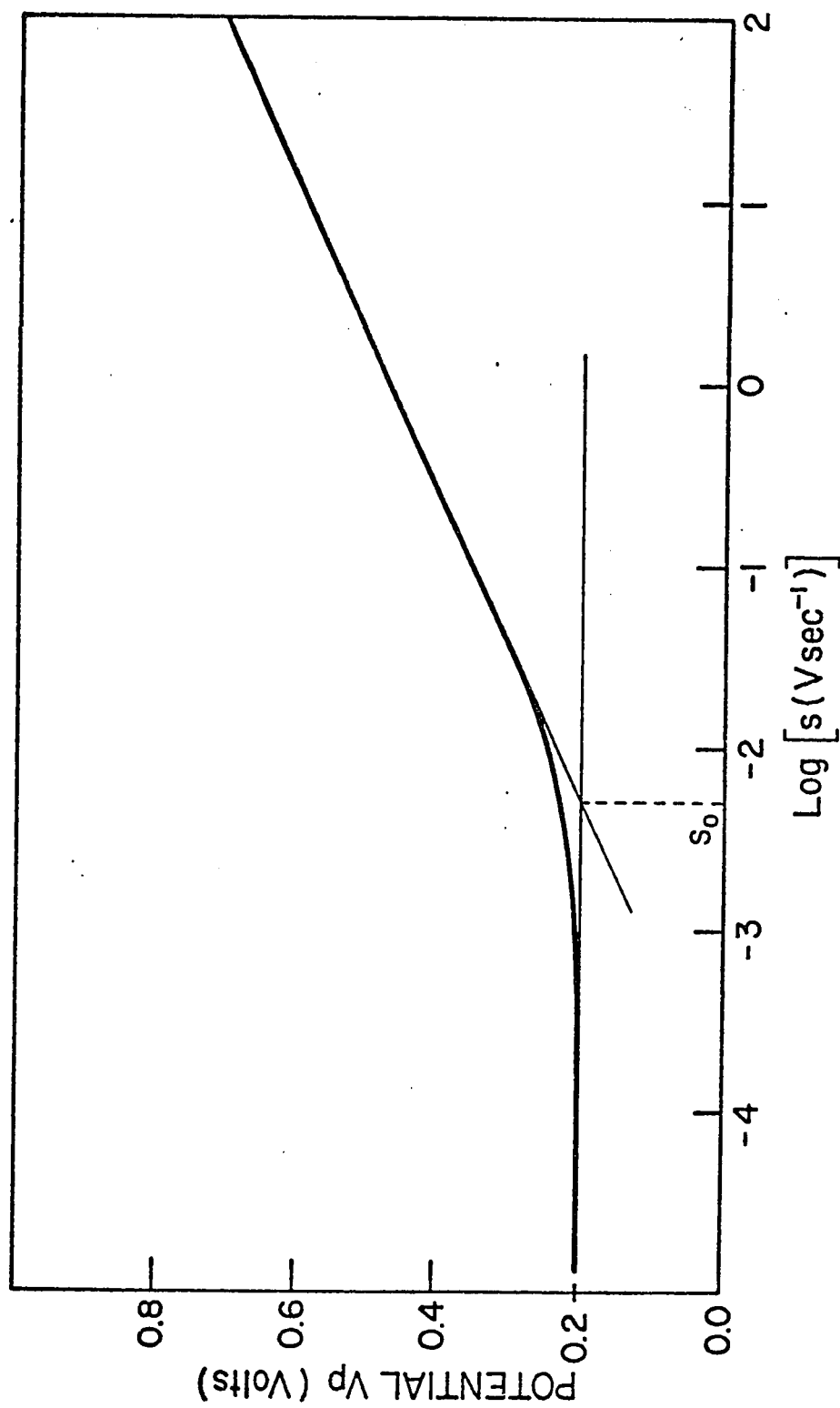


Fig. 9-4 Plot of V_p as a function of $\log s$ showing the transition from reversible to irreversible behaviour of inhibiting step [1] of reaction mechanism (VIII).

- Fig. 9-2) with change of sweep-rate under conditions when process [1] remains reversible then the rate constant k_2' cannot be determined from the exchange current value. When such conditions prevail, then from the irreversible i - V curves alone, only the Tafel slope and an apparent $i_{o,2}$ value can be calculated. The value of k_2' may, however, be determined if the peak current $i_{1,p}$ is known for the 1-e electrochemical reaction [1], or in general for any inhibiting reaction under irreversible conditions. Then, using eqn. (9-6), where i_1 is now taken as $i_{1,p}$ and i_{Tot} is equal to $i_{Tot,p}$, the rate constant k_2' for the Faradaic process may be evaluated. The values of k_1 and $\Delta E^\circ (=E_1^\circ - E_2^\circ)$ are assumed to be known from the calculations referred to in procedures (a), (b) and (d) above;
- (f) Finally, it may be noted that no kinetic information can be obtained in the present analysis for reaction [3] because this reaction is assumed to be very rapid in this scheme and is hence not a rate-determining step in the overall Faradaic process.

CHAPTER X

MONOLAYER FORMATION BY A NUCLEATION AND GROWTH MECHANISM

10.1 Introduction

In Chapter I, Part 1.6, it was pointed out that growth of a monolayer could occur not only by the random deposition of particles on a lattice of sites on a substrate surface (Langmuir model), but also alternatively by lateral growth from nuclei formed, or initially present, on a surface. These nuclei are usually groups of neighbouring atoms on a surface plane or other defects in the substrate surface. The two mechanisms are basically different, so it is of interest and importance to be able to distinguish when one or other of them is involved in a kinetic study of monolayer growth.

Since much of the existing experimental work on monolayer growth and stripping has been carried out by the potentiodynamic method, it is necessary to establish criteria by which a nucleation and growth mechanism, if it were involved, could be recognized in the current-potential response generated by a potential sweep.

In the present chapter, therefore, the current-potential (i-V)* profiles will be examined which result from application of a

* In a number of places in this chapter, the terms "C-V profiles" and "i-V profiles" have been used interchangeably. As in previous cases discussed, the C-V profiles are simply plots of reduced currents, i/s , and thus have the units of capacitance per cm^2 .

linear potential sweep to an electrode at which nucleation of two-dimensional growth or removal of an ad-layer by a similar process of nucleation of holes can occur. The diagnostic features of the potential-sweep behaviour for these mechanisms which will be of interest are:

(a) the shapes of the i - V profiles, (b) their dependence on sweep-rate, (peak potentials and peak currents) and (c) the half-width⁹³ of the i - V profiles. Comparisons with the results for a regular surface process (cf. ref. 90 and Chapter IV) occurring at random with no nucleation control will be made.

The characteristic forms of potentiodynamic current-potential profiles for a simple 1-electron surface reaction have been previously treated in Chapter IV in relation to the results of other authors⁹⁰. In such processes, random electrodeposition or desorption of the electro-active species occurs at a rate controlled by (a) coverage θ or free area $1-\theta$, (b) potential V in the sweep and (c) the value of any interaction or surface heterogeneity factor g ^{31,33}.

The investigation of nucleation-controlled growth of electro-deposits cannot conveniently or practically be made by steady-state techniques. A.C. impedance, galvanostatic and potentiostatic pulse methods have therefore been employed (see Chapter I, Part 1.6) but no analysis has been made of the potentiodynamic current-potential profiles corresponding to formation of a surface layer by a nucleation and growth process. Such a two-dimensional surface process can be deposition of a species up to a monolayer or desorption of a species, e.g., in reduction of a surface oxide or electrochemical oxidative desorption of metallic monolayers.

Features which distinguish nucleation and growth in monolayer formation from random electrodeposition (Langmuir case) treated in Chapter IV will be emphasized.

Two main mechanisms will be considered: one where the growth occurs from a fixed surface density of nuclei and the other where growth occurs from a potential-dependent density of nuclei. Computer simulations and some analytical derivations of the kinetic behaviour for these two cases are made and the characteristic kinetic features of the process for the two conditions and two mechanisms are deduced, enabling the latter to be distinguished in terms of experimentally accessible criteria.

The extent of reversibility of the processes can be usefully expressed in terms of a limiting sweep-rate parameter, s_0 , which is related to the rate constants for nucleation or growth and the surface density of nuclei.

The kinetic behaviour of a surface process involving the deposition of a two-dimensional surface film by a nucleation and growth mechanism under potentiostatic step control conditions will also be treated for comparison, since the latter method has some advantages if it is known that a nucleation and growth mechanism is involved.

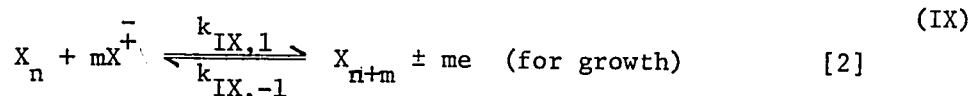
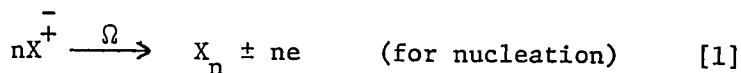
10.2 Model to which Simulation Calculations are Applied

The growth process in two dimensions is assumed to proceed from a number of nuclei in a series of expanding circles which eventually overlap, the growth continuing at the remaining perimeters of the non-

overlapping parts of the circles. Such a model was employed by Evans¹¹⁵ in his treatment of grain-size of metals and development of surface films of corrosion products on metal surfaces. The procedure of Evans was used and adapted to the case of electrochemical surface reactions.

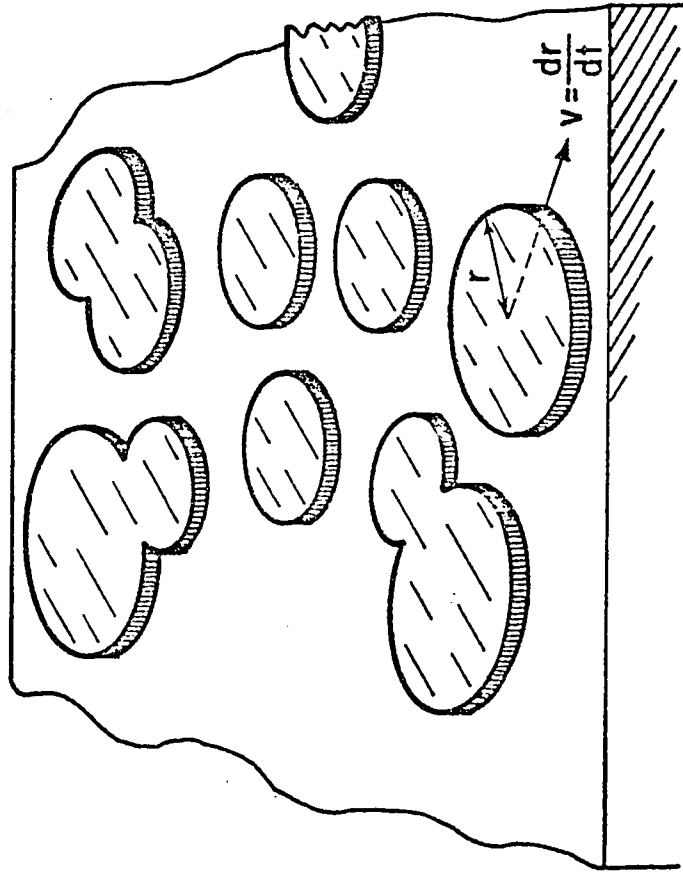
The model can be applied to the development of a monolayer of a new phase by an "island growth process" (Fig. 10-1a) or to the electrochemical removal (stripping) of species from an initial monolayer by a "lake growth process" (Fig. 10-1b). The two cases are mathematically identical except that for the stripping case in the text to follow, θ should be identified with the fraction of the surface on which holes have been generated.

The following reaction mechanism (IX), consisting of two processes, is considered:



where X^+ represents the species in solution, n and m are the number of species involved in each reaction step. X_n is the number of species X deposited on the surface in a nucleus of critical size which can grow and X_{n+m} is the number of species deposited on the surface at a given time after growth of the critical nucleus has started. Reaction processes [1] and [2] are: (a) electrochemical steps involving cathodic deposition of metal atoms or anodic formation of a film, or (b) generation of holes in an existing film.

(a) Film Growth



(b) Film Stripping

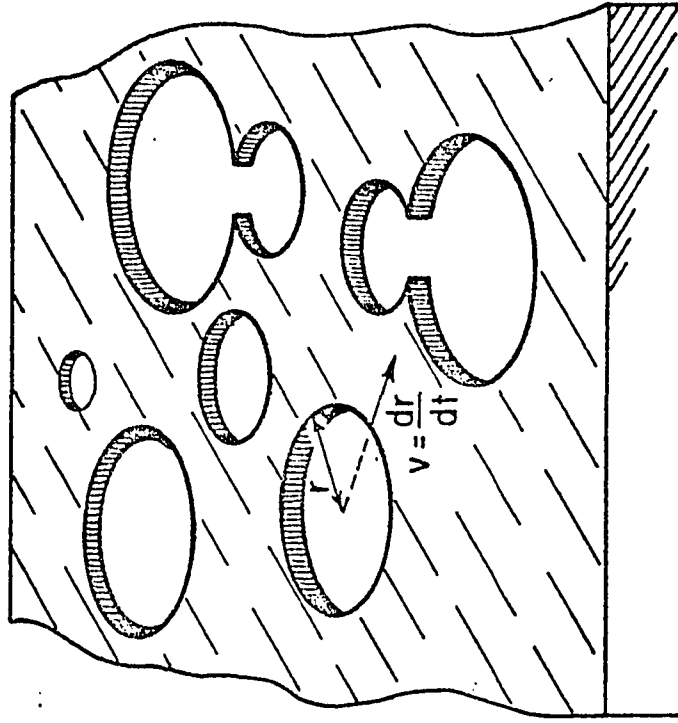


Fig. 10-1 Models for growth of (a) islands of a deposited species or (b) holes or "lakes" in a previously complete monolayer.

The case of a 1-electron anodic process will be considered in the derivations to follow. It will be assumed that the electrochemical reactions are rate-determining, i.e., no diffusion limitation exists. The concentration of the species in solution $X^{\pm}$ will be taken as 1 mol l⁻¹ and included for convenience in the rate constants (see footnote p.96). It is assumed that nucleation occurs randomly on the surface and n(=1) is the number of atoms in a nucleus. Taking a more realistic model of several atoms (cf. ref. 117) in a nucleus will introduce only a small change in the scale of reversible potential to which the potential V in eqn. (10-1) is referred. The reversible potential for nuclei will strictly vary continuously with added atoms until the value for the complete two-dimensional phase is attained but probably a nucleus can already meaningfully be defined as 2 or 3 atoms¹¹⁷. Choice of n=1 greatly facilitates the mathematical representation and solution of problems to be considered below and will not significantly affect the forms of potentiodynamic profiles to be calculated for various conditions of the subsequent growth at nuclei. Then the nucleation rate j which is proportional to the free surface (1-θ) is

$$j = \frac{dN}{dt} = \Omega(1-\theta) \exp\left(\frac{V}{b}\right) \quad (10-1)$$

where Ω is a normalized nucleation rate parameter [including unit concentration (see footnote p. 96)] expressed in number of nuclei cm⁻² sec⁻¹, N is the number of nuclei on 1 cm² of the surface, θ is the fraction of the surface which is covered and $b = \frac{RT}{\beta F}$; also R,T,F,t,V and β have their usual meanings (cf. Chapter IV, Part 4.2). In eqn. (10-1)

the back-reaction of the nucleation process can be neglected because θ_N , the fraction of the surface covered by nuclei, is extremely small in comparison with θ .

The growth rate of a circle in mol sec^{-1} at which deposition is occurring, $w = \frac{dM}{dt}$, will be proportional to the number of moles M placed on the surface phase boundary per unit time, i.e., at the circumference $2\pi r$ of the growing circles; thus, for $\beta = 0.5$

$$w = \frac{dM}{dt} = \frac{2\pi r}{\delta N_A} [k_1 \exp(\frac{V}{b}) - k_{-1} \exp(-\frac{V}{b})] \quad (10-2)$$

where δ is the diameter of deposited particles assumed to be spheres, k_1 and k_{-1} are the forward* and backward rate constants of the growth reaction [2] and N_A is Avogadro's number. The current density, i , for the growth process is then

$$i = Q \frac{d\theta}{dt} = zFwN, \quad (10-3)$$

Q being the charge for monolayer formation and z is the number of electrons exchanged in the reaction (taken as 1). The time-dependence of θ due to growth of randomly generated, expanding circles of the electrodeposited species is given from the basic equation of Evans¹¹⁵ using the concept of expectation number $\bar{E}$. In Evans' method, Poisson's formula is used to calculate the statistical random distribution of growing circles and the probability P that a given point on the surface is not covered. This probability is directly related to the fraction of the free surface, $1-\theta$, i.e.,

* For convenience, k_1 will contain unit concentration of $X^{\pm}$ in solution (see footnote, p. 96) and is thus a rate parameter rather than a rate constant.

$$1 - \theta = P = \exp(-\tilde{E}) \quad (10-4)$$

and

$$\theta = 1 - \exp(-\tilde{E}) \quad (10-5)$$

Then, using eqn. (10-3), the current density is obtained as

$$i = Q \frac{d\theta}{dt} = Q \exp(-\tilde{E}) \frac{d\tilde{E}}{dt} \quad (10-6)$$

$\tilde{E}$ is found by integrating all the elementary contributions, $d\tilde{E}$, due to annuli of breadth dr situated around a nucleus at radial distances r where $d\tilde{E}$ is defined as

$$d\tilde{E} = N 2\pi r dr \quad (10-7)$$

The integration is made over all values of r from zero to $r = \int_0^t v dt$, where v is the radial velocity of growth of the expanding circles given by

$$v = \frac{dr}{dt} = \alpha [k_1 \exp(\frac{V}{b}) - k_{-1} \exp(-\frac{V}{b})] \quad (10-8)$$

In this equation, α is a factor related to the size of deposited atoms in cm which converts rate of deposition (terms in square brackets) to radial rate of circle growth. As will be shown later, it can easily be calculated from the potentiostatic case (see p.190). It enables the rate of growth expressed by the term in square brackets in eqn. (10-8) in sec^{-1} to be converted to a radial growth rate expressed by v in cm sec^{-1} .

The process of nucleation and growth is, of course, potential-dependent as can be seen from eqns. (10-1) and (10-2). Various cases

can therefore be developed, depending on experimental conditions for monolayer formation. The behaviour under (i) potentiostatic ($V = \text{constant}$) and (ii) potentiodynamic ($\frac{dV}{dt} = \text{constant}$) growth conditions will be discussed here for the cases of:

- (a) constant initial number of nuclei N_0 , $j = 0$;
- (b) potential-dependent number of nuclei N_V , $j = f(V)$;
- (c) or the special condition where the number of nuclei increases in a potential-dependent way from a certain initial number of nuclei N_0 present on the surface to a number $N = N_0 + N_V$.

Practically, the cases of importance are growth from nuclei which are generated at a potential-dependent rate j , and growth from an initially established density of nuclei, N_0 , with continuing generation of nuclei at the rate j .

10.3 Calculation Procedure and Values of Parameters

Numerical calculations for the various cases considered above were carried out on an IBM 360, model 65, computer using the "System/360 Continuous System Modeling Program" - S/360 CSMP as in all the other computations of the various reaction mechanisms studied. Again, the fourth-order Runge-Kutta method was employed to solve the differential equations pertaining to the reaction mechanism (IX). Various values of rate constants and other parameters were used. While they were chosen arbitrarily but in reasonable ranges in relation to experimental behaviour, the main purpose of the calculations was to establish the

forms of current-potential and current-time relations, and to derive properties of the curves which are independent of arbitrarily chosen values of parameters.

In all the calculations, the total number of available sites, N_s , per cm^2 of surface was taken as 10^{15} , which corresponds to $Q = 160 \text{ } \mu\text{C cm}^{-2}$ and to δ , the diameter of the adsorbed species, being $\delta = \left(\frac{1}{N_s}\right)^{1/2} = 3.162 \times 10^{-8} \text{ cm}$, assuming a (100)-plane geometry of the substrate surface. The conversion factor α which arises in eqn. (10-8) will then be $\alpha = \frac{1}{N_s \delta} = 3.162 \times 10^{-8} \text{ cm}$ according to eqn. (10-23) (see below). The value of the rate constants for reaction [2], $k_1 = k_{-1}$, is chosen such that $(k_1)^2 = 1.0 \times 10^{-3}$ which gives $k_1 = k_{-1} = 3.162 \times 10^{-2} \text{ sec}^{-1}$ and $\alpha k_1 = 1.0 \times 10^{-9} \text{ cm sec}^{-1}$. In most cases, the values for N_0 and Ω are selected so that the number of nuclei on the surface in cases (a) and (b) remain of similar order during most of the formation of the monolayer. The potential scale is defined with respect to the reversible potential E_r of the growth process taken as zero as a reference value. The activity of the species deposited in the growing circles is assumed to be unity, as for bulk material, so that E_r is independent of circle radius. Thus the potential V is numerically equal to the overpotential η . The standard electrode potential, E_{nuc}° , for the random deposition process of nuclei (reaction step [1]) and the initial potential, V_{in} , in a sweep are both taken equal to $E_r (=0; \text{see above})$.

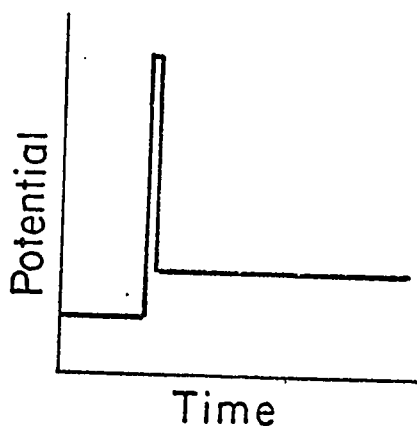
10.4 Growth from an Initially Established Density of Nuclei, N_0 -

Case (I)

10.4.1 Potentiostatic conditions - Case (I-1)

10.4.1.1 Formulation of an expression for the current density

This case will correspond to the following potential programme imposed on the electrode:



The initial conditions are:

$$\text{at } t = 0, \quad N = N_0$$

$$r = 0$$

and during the process of growth

$$j = 0, \quad V = \text{constant}, \quad v(V) = \text{constant}$$

Eqn. (10-7) can now be integrated taking into account that, from eqn. (10-8),

$$dr = v \, dt \tag{10-9}$$

and

$$r = vt \quad (10-10)$$

Hence

$$\tilde{E} = 2\pi N_o \int_0^{r(t)} r dr = 2\pi N_o v^2 \int_0^t t dt \quad (10-11)$$

The integration can be performed, viz.

$$\tilde{E} = \pi N_o v^2 t^2 \quad (10-12)$$

so that the current density can be calculated from eqns. (10-6), (10-11) and (10-12) as

$$i = Q2\pi N_o v^2 t \exp(-\pi N_o v^2 t^2) \quad (10-13)$$

10.4.1.2 Calculation of the current peak parameters

For interpretation of results obtained for surface processes it is usually useful to evaluate the properties of the transient at its peak.

For small t , when $\pi N_o v^2 t^2 \ll 1$, eqn. (10-13) can be approximated by

$$i = Q2\pi N_o v^2 t (1 - \pi N_o v^2 t^2 + \dots) \doteq Q2\pi N_o v^2 t \quad (10-14)$$

i.e., at the beginning of circle growth, before overlap occurs, the current density is proportional to time. However, when the circles begin to overlap, the current will increase more slowly and with more circles overlapping it will eventually diminish giving rise to a peak on an i - t plot (Fig. 10-2). It can be shown that the maximum current

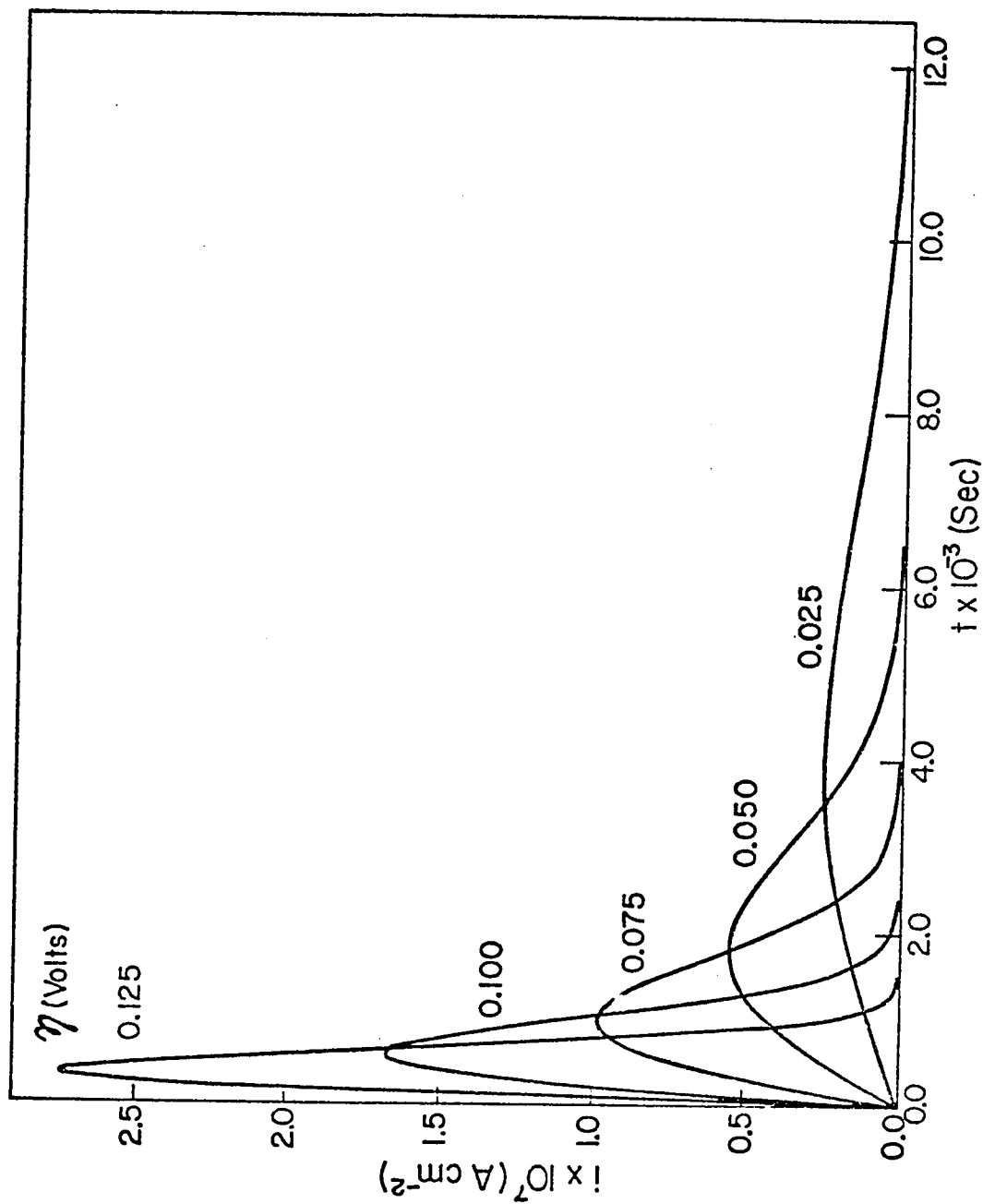


Fig. 10-2 Family of current-time (i-t) profiles for a nucleation and growth process at various overpotentials for the case where the density of nuclei N_0 does not change with time or potential; $N_0 = 10^{10} \text{ cm}^{-2}$.

density i_p is inversely proportional to the time t_p , at which the maximum occurs after initiation of the growth process.

At the peak, $\frac{di}{dt} = 0$; thus by differentiating eqn. (10-13) and equating the result to 0 for $t = t_p$

$$1 - 2\pi N_o v^2 t_p^2 = 0 \quad (10-15)$$

is obtained, from which

$$t_p = \left(\frac{1}{2\pi N_o v^2} \right)^{1/2} \quad (10-16)$$

and by substituting t_p in eqn. (10-13) the corresponding peak current density can be found as

$$i_p = Q(2\pi N_o v^2)^{1/2} \exp\left(-\frac{1}{2}\right) = \frac{Q \exp\left(-\frac{1}{2}\right)}{t_p} \quad (10-17)$$

It can be seen that

$$i_p t_p = \text{constant} = 0.607 Q \quad (10-18)$$

The coverage, θ , for this case can be found from eqns. (10-5) and (10-12) as

$$\theta = 1 - \exp(-\pi N_o v^2 t^2) \quad (10-19)$$

Then, for $t = t_p$, the interesting result is found that the coverage to the peak θ_p is constant, independent of the number of nuclei and of the growth rate:

$$\theta_p = 1 - \exp\left(-\frac{1}{2}\right) = 0.394 \quad (10-20)$$

From eqns. (10-18) and (10-20), it is evident that the product $i_p t_p$ and the charge to the peak expressed as θ_p is always the same, regardless of the state of reversibility in reaction [2].

10.4.1.3 Calculation of the conversion factor α [eqn.(10-8)]

The conversion factor α can be easily calculated by considering the conditions for small t and expressing the current density by eqns. (10-3) and (10-14), taking $z = 1$,

$$i = FwN_o = Q2\pi N_o v^2 t \quad (10-21)$$

Substituting w from eqn. (10-2) and taking in account that $r = vt$ as well as using v from eqn. (10-8) enables

$$F \frac{2\pi r}{\delta N_A} [k_1 \exp(\frac{V}{b}) - k_{-1} \exp(-\frac{V}{b})] = Q2\pi r \alpha [k_1 \exp(\frac{V}{b}) - k_{-1} \exp(-\frac{V}{b})] \quad (10-22)$$

to be obtained from which

$$\alpha = \frac{F}{Q} \frac{1}{\delta N_A} = \frac{1}{N_s \delta} \quad (10-23)$$

$1/N_s$ being the area in cm^2 of a deposited atom on the surface.

Assuming sphericity of deposited atoms and a (100) substrate plane,

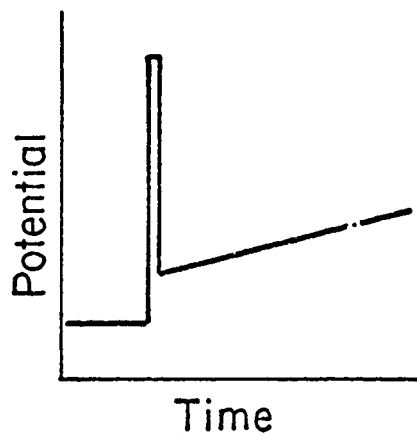
$\frac{1}{N_s} = \delta^2$, so that

$$\alpha = \delta \quad (10-24)$$

10.4.2 Potentiodynamic conditions - Case (I-2)

10.4.2.1 Formulation of an expression for the current density

This case corresponds to the following potential programme imposed on the electrode:



Eqn. (10-7) will now be integrated for the following conditions:

$$\text{for } t = 0$$

$$N = N_0$$

$$r = 0$$

and

$$j = 0$$

For the case of an anodic-going sweep, the modulating potential, ΔV , which is equal to the overpotential, η , is given by

$$\Delta V = V_{in} + st - E_r = \eta \quad (10-25)$$

where $V_{in}(=0)$ is the initial potential in the sweep at a rate $s = \frac{dV}{dt}$ and E_r is the reversible potential of the growth process (see definition on p.186).

The potential-dependent radial rate of growth of circles in this case is written from eqn. (10-8) as

$$v = \frac{dr}{dt} = \alpha [k_1 \exp(\frac{\eta}{b}) - k_{-1} \exp(-\frac{\eta}{b})], \quad (10-26)$$

Eqn. (10-7) has the form

$$\tilde{E} = 2\pi N_o \int_0^t v(\int_0^t v dt) dt \quad (10-27)$$

and the current density is given by

$$i = Q2\pi N_o v(\int_0^t v dt) \exp[-2\pi N_o \int_0^t v(\int_0^t v dt) dt] \quad (10-28)$$

Eqn. (10-28) cannot be integrated analytically. However, numerical integration can be easily performed and results are shown in Fig. 10-3 where the derived currents are shown in terms of the pseudocapacitance $C(= \frac{i}{s})$ plotted as a function of potential for various values of the reduced sweep-rate $\frac{1}{N_o} (\frac{s}{k_1})^2$, which is, as was shown earlier (see Chapter IV), a measure of the extent to which the reaction is driven to a condition of irreversibility.

10.4.2.2 Calculation of the current peak parameters

The values of the peak potential, V_p , coverage to the peak, θ_p , and the pseudocapacitance at the peak, C_p , can be determined

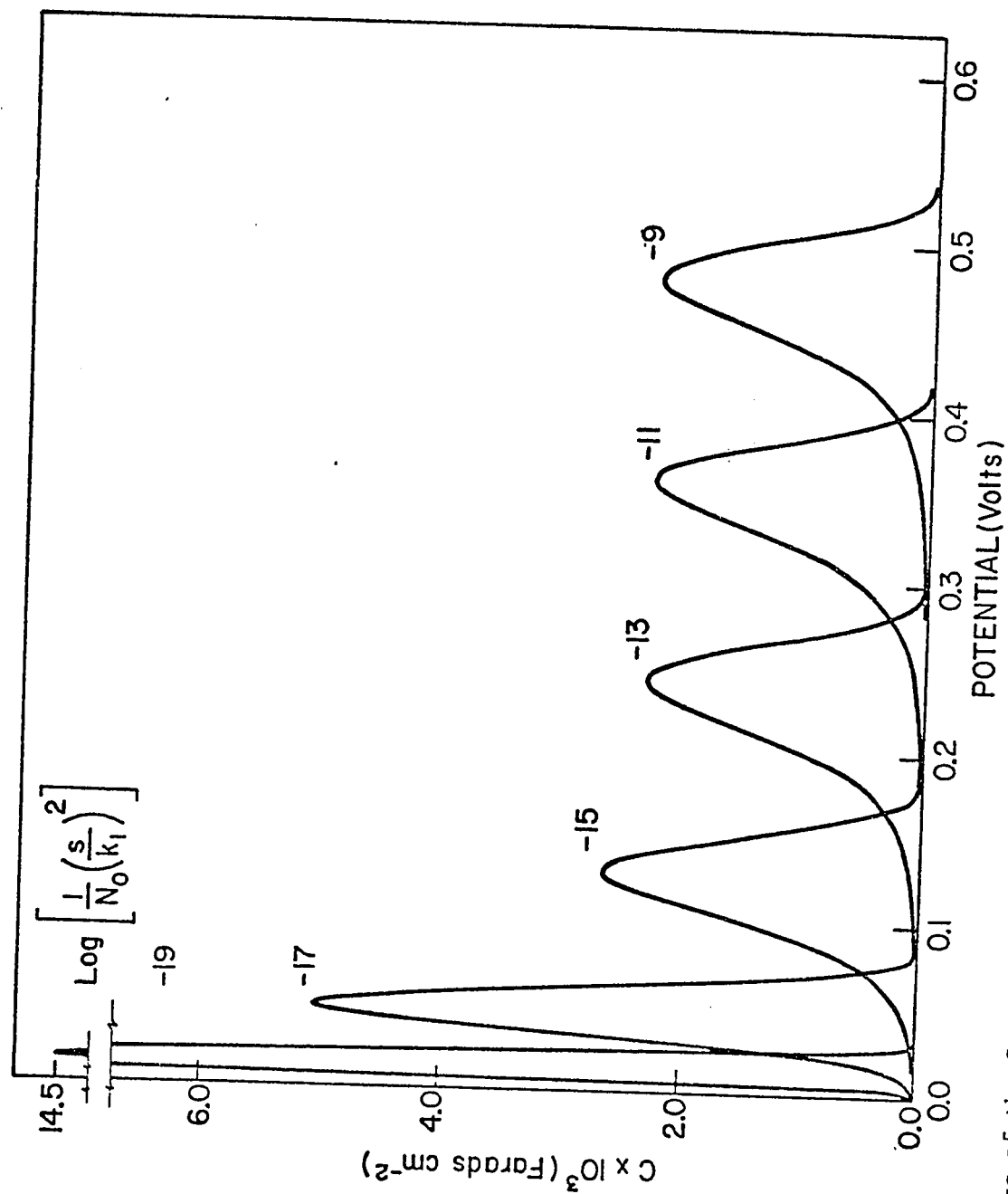


Fig. 10-3 Plots of the C vs. V profiles for a nucleation and growth process for various values of the reduced sweep-rate parameter $\frac{1}{N_o} \left(\frac{s}{k_1} \right)^2$. The density of nuclei does not change with changing overpotential η and time t .

analytically for conditions under which the sweep-rate s is large enough to drive the reaction [2] to a condition of irreversibility; then the back-reaction in eqn. (10-26) can be neglected, which make the analytical integration of the first integral in eqn. (10-27) possible:

$$\int_0^t v \, dt = \alpha k_1 \frac{b}{s} \exp\left(-\frac{V_{in} - E}{b}\right) \left[\exp\left(\frac{st}{b}\right) - 1\right] \quad (10-29)$$

For irreversible conditions, $\exp\left(\frac{st}{b}\right) \gg 1$; hence eqn. (10-29) can be simplified to

$$\int_0^t v \, dt = \alpha k_1 \frac{b}{s} \exp\left(\frac{\eta}{b}\right) \quad (10-30)$$

By substituting eqn. (10-30) into (10-27) and integrating again, the expectation number is obtained:

$$\tilde{E} = \pi N_0 \alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 \exp\left(\frac{2\eta}{b}\right) \quad (10-31)$$

The current density can then be calculated from eqns. (10-6) and (10-31) as

$$i = Q 2 \pi N_0 \alpha^2 k_1^2 \frac{b}{s} \exp\left(\frac{2\eta}{b}\right) \exp\left[-\pi N_0 \alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 \exp\left(\frac{2\eta}{b}\right)\right] \quad (10-32)$$

In order to determine the peak values V_p , θ_p , and C_p , eqn. (10-32) is differentiated w.r.t. time t giving, for the behaviour at the peak:

$$\begin{aligned} \frac{di}{dt} = 0 = Q 2 \pi N_0 \alpha^2 k_1^2 \frac{b}{s} \exp\left(\frac{2\eta}{b}\right) \exp\left[-\pi N_0 \alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 \exp\left(\frac{2\eta}{b}\right)\right] \\ \left[\frac{2s}{b} - 2 \pi N_0 \alpha^2 k_1^2 \frac{b}{s} \exp\left(\frac{2\eta}{b}\right)\right] \end{aligned} \quad (10-33)$$

From this equation, the potential V_p for the peak is readily obtained as

$$V_p - E_r = b \ln \frac{s}{bk_1} - b \ln \alpha - \frac{1}{2} b \ln \pi N_o \quad (10-34)$$

The dependence of V_p on sweep-rate s is seen to be the same (see Chapter IV, Fig. 4-2) as for the 1-electron surface reaction (Langmuir case irreversible conditions), viz. the V_p will shift 0.118 V per decade of change of s (Fig. 10-4).

The coverage to the peak, θ_p , can be found by substituting eqn. (10-34) into (10-31). Thus, the result $\tilde{E}_p = 1$ is obtained and hence

$$\theta_p = 1 - \exp(-\tilde{E}) = 1 - \exp(-1) = 0.632 \quad (10-35)$$

Also, substituting eqn. (10-34) into (10-32), the corresponding i_p can be determined as

$$i_p = \frac{2 Qs \exp(-1)}{b} = 0.368 \frac{QFs}{RT} \quad (10-36)$$

or

$$C_p = \frac{2 Q \exp(-1)}{b} = 0.368 \frac{QF}{RT} \quad (10-37)$$

which is twice the value of C_p for the 1-electron irreversible surface reaction³³ under Langmuir conditions. The dependence on the peak parameters on the reduced sweep-rate is shown in Fig. 10-4.

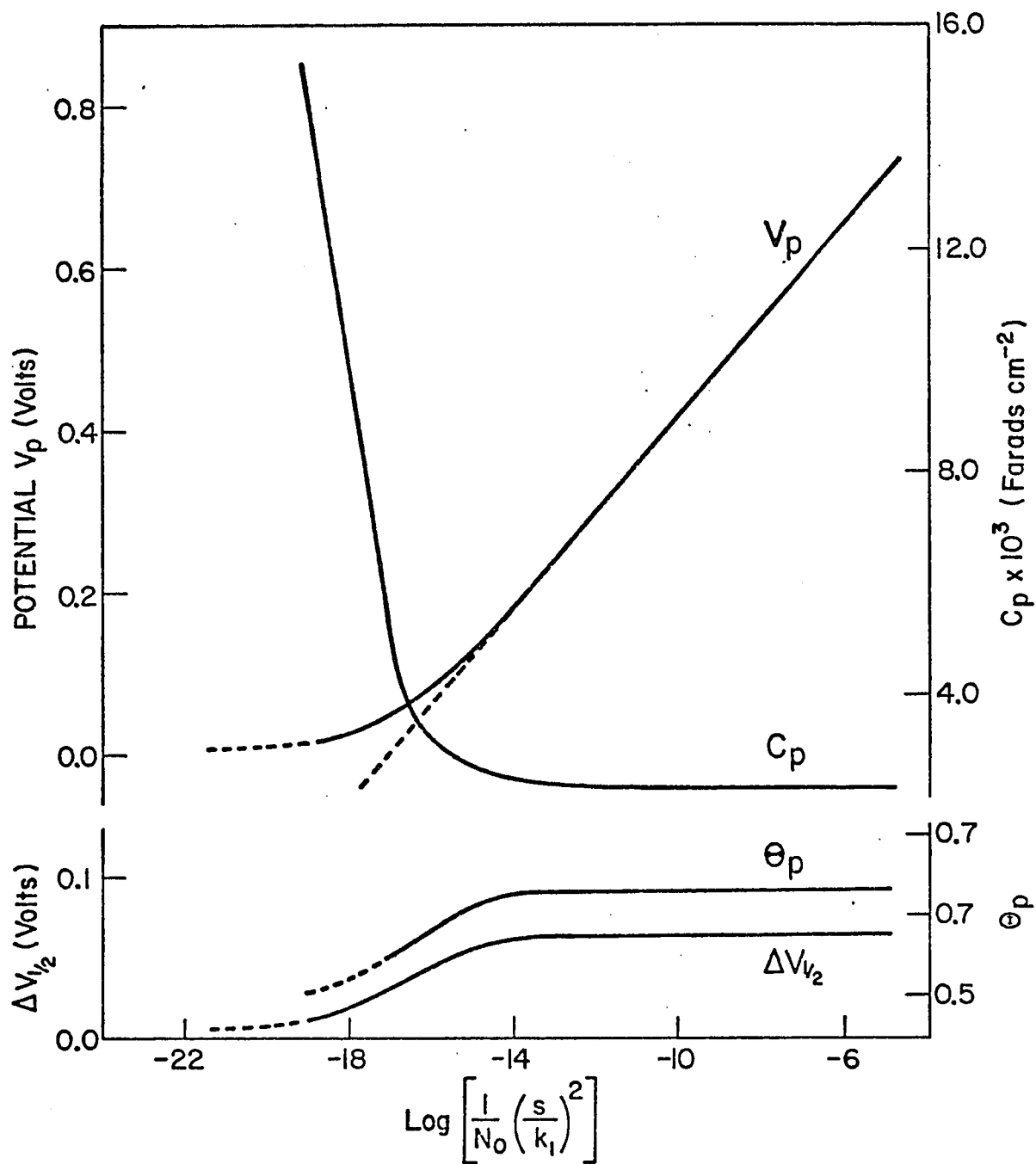


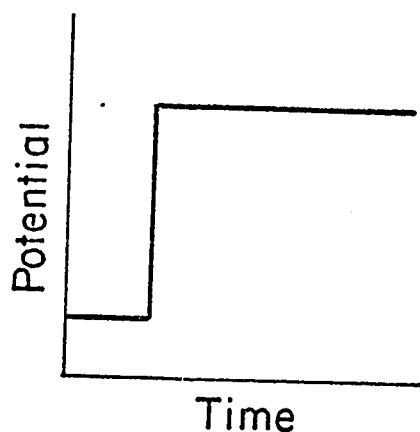
Fig. 10-4 Plots of peak parameters V_p , C_p and θ_p together with $\Delta V_{1/2}$ as a function of the reduced sweep-rate parameter $\log \frac{1}{N_0} \left(\frac{s}{k_1} \right)^2$ for constant density of nuclei, N_0 , [Case (I-2)].

10.5 Growth from a Density of Nuclei which Varies as a Function of Potential and Time - Case (II)

10.5.1 Potentiostatic conditions - Case (II-1)

10.5.1.1 Formulation of an expression for the current density

The potential imposed on the electrode will have to be high enough for nucleation and growth to occur simultaneously, as shown schematically below:



For this case, the conditions for integration of eqn. (10-7) are:

$$\text{for } t = 0 \quad N = 0$$

$$r = 0$$

and

$$V = \text{constant}$$

$$\Omega'(V) = \Omega \exp\left(\frac{V}{b}\right) = \text{constant} \quad (10-38)$$

$$v(V) = \text{constant}$$

Eqn. (10-7) will be written

$$\tilde{E} = 2\pi \int_0^t \left(\int_0^{r(t)} r dr \right) j dt \quad (10-39)$$

which after first integration and substitution of eqns. (10-1), (10-9) and (10-10) into (10-39) gives

$$\tilde{E} = \pi \int_0^t r^2 j dt = \pi \Omega' v^2 \int_0^t t^2 (1-\theta) dt \quad (10-40)$$

The current density i from eqn. (10-6) can then be written

$$i = Q\pi\Omega' v^2 t^2 (1-\theta) \exp[-\pi\Omega' v^2 \int_0^t t^2 (1-\theta) dt] \quad (10-41)$$

Eqn. (10-41) can be solved analytically as follows: The differential of eqn. (10-40) is

$$d\tilde{E} = \pi\Omega' v^2 t^2 (1-\theta) dt \quad (10-42)$$

Substituting eqn. (10-5) into (10-42), rearranging and integrating both sides and applying the boundary condition $\tilde{E}=0$ at $t=0$ gives

$$\exp(-\tilde{E}) = \frac{3}{3 + \pi\Omega' v^2 t^3} = 1 - \theta \quad (10-43)$$

and

$$\theta = \frac{\pi\Omega' v^2 t^3}{3 + \pi\Omega' v^2 t^3} \quad (10-44)$$

Differentiating eqn. (10-44) and substituting it in eqn. (10-3) for the current density,

$$i = Q \frac{9\pi\Omega' v^2 t^2}{(3 + \pi\Omega' v^2 t^3)^2} \quad (10-45)$$

is obtained.

The potentiostatic i - t profiles which can be obtained either numerically [eqn. (10-41)] or analytically [eqn. (10-45)] are shown in Fig. 10-5 for various values of the overpotential, η .

10.5.1.2 Calculation of the current peak parameters

The peak quantities i_p , t_p and θ_p are determined in the usual way by differentiating eqn. (10-45), i.e.,

$$\frac{di}{dt} = 0 = Q \frac{18 \pi \Omega' v^2}{(3 + \pi \Omega' v^2 t^3)^3} (3t - 2\pi \Omega' v^2 t^4) \quad (10-46)$$

The condition of eqn. (10-46) being zero is satisfied by either:

(i) $t=0$ giving $i=0$ which corresponds to initial conditions;

or

$$(ii) \quad t_p = \left(\frac{3}{2\pi \Omega' v^2} \right)^{1/3} \quad (10-47)$$

for the maximum current density i_p . i_p is obtained by substituting eqn. (10-47) into (10-45):

$$i_p = \frac{2}{3} Q \left(\frac{2\pi \Omega' v^2}{3} \right)^{1/3} = \frac{2}{3} \frac{Q}{t_p} \quad (10-48)$$

A general relation as for the preceding potentiostatic case, [eqn. (10-18)], is obtained for the $i_p t_p$ product from eqns. (10-47) and (10-48); thus

$$i_p t_p = \frac{2}{3} Q \quad (10-49)$$

and from eqns. (10-47) and (10-44) for the coverage to the peak

$$\theta_p = \frac{1}{3} \quad (10-50)$$

As before, these two values are independent of kinetic parameters of the reaction.

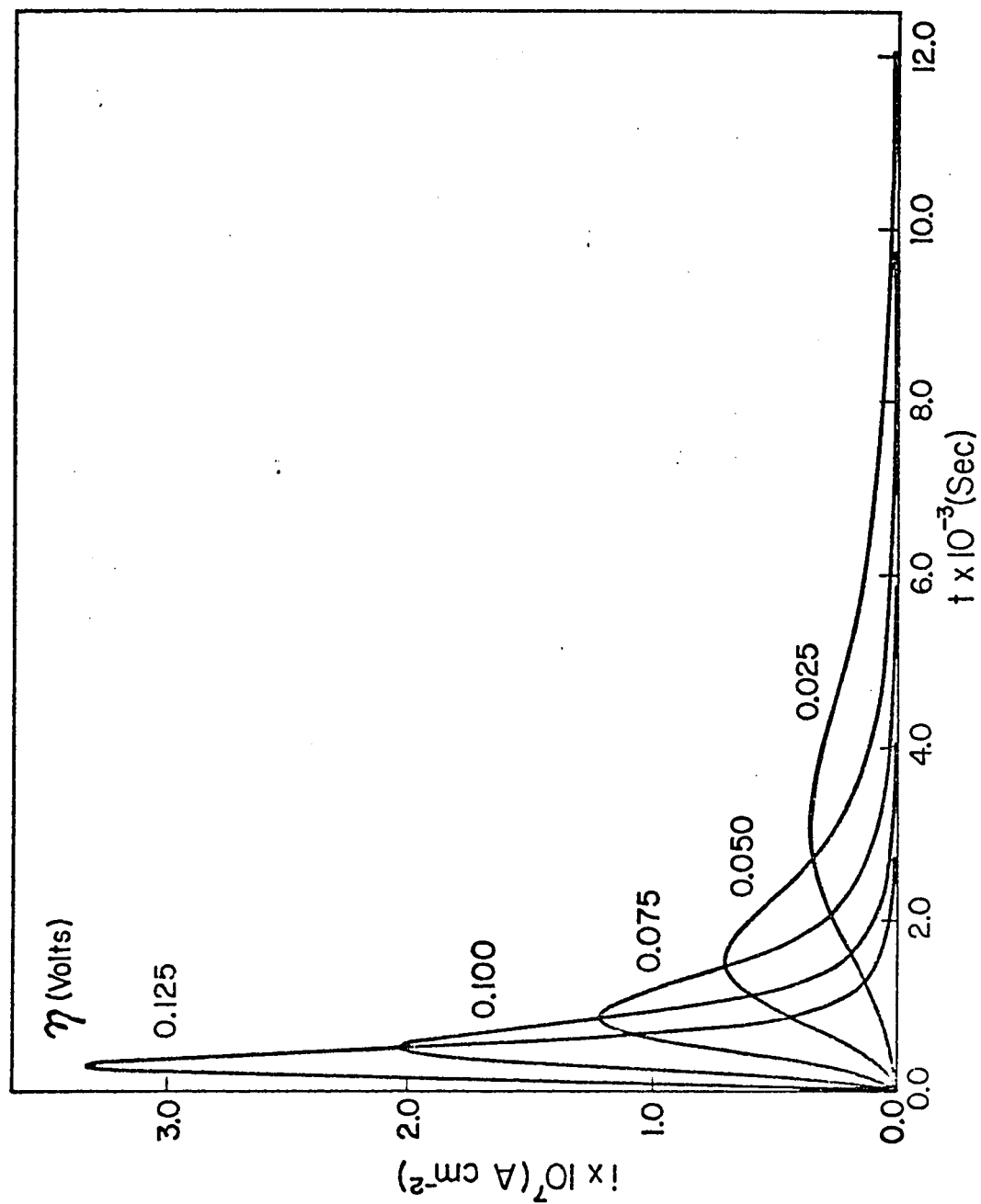
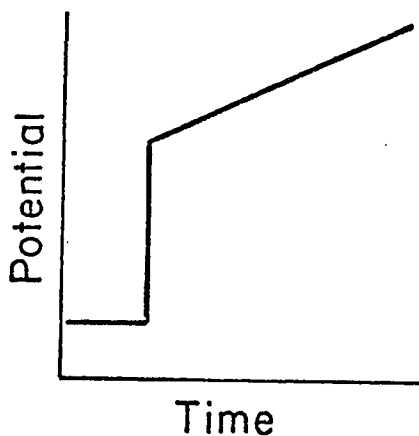


Fig. 10-5 Simulation of i - t profiles for a nucleation and growth process at various overpotentials for the case where the density of nuclei changes with time with a rate constant $\Omega = 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$, [Case (II-1)].

10.5.2 Potentiodynamic conditions - Case (II-2)

10.5.2.1 Formulation of an expression for the current density

For this case, the potential programme will be as follows:



and the conditions for integration of eqn. (10-7), which will have the form

$$E = 2\pi \int_0^t \left(\int_0^{r(t)} r dr \right) j dt \quad (10-39)$$

are:

$$\text{for } t = 0 \quad N = 0$$

$$r = 0$$

and $j = f(V)$

$$v = f(V)$$

$$\Delta V = V_{in} + st - E_r = \eta \quad (10-25)$$

After integration of eqn. (10-39) with respect to r and substitution

of eqn. (10-1) for j, the equation for the expectation number is

$$\bar{E} = \pi\Omega \int_0^t \left(\int_0^t v dt \right)^2 (1-\theta) \exp\left(\frac{\eta}{b}\right) dt \quad (10-51)$$

and from eqns. (10-51) and (10-6), the current density is given by

$$i = Q\pi\Omega(1-\theta)\exp\left(\frac{\eta}{b}\right) \left(\int_0^t v dt \right)^2 \exp\left[-\pi\Omega \int_0^t (1-\theta)\exp\left(\frac{\eta}{b}\right) \left(\int_0^t v dt \right)^2 dt\right] \quad (10-52)$$

which can only be solved numerically. The results of the numerical integration are plotted in Fig. 10-6 as C versus V for various values of the reduced sweep-rate which, for this case, is $\frac{s^3}{\Omega k_1^2}$.

For conditions under which the sweep-rate s is sufficiently large to drive the reaction [2] to a condition of irreversibility, the back-reaction in eqn. (10-26) may obviously be neglected. The integration of the inner integral in eqn. (10-51) then becomes possible yielding the result given by eqn. (10-30) (p.193). Substituting eqn. (10-30) into (10-51) gives:

$$\bar{E} = \pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 \int_0^t (1-\theta) \exp\left(\frac{3\eta}{b}\right) dt \quad (10-53)$$

and from eqns. (10-6) and (10-53) the current density

$$i = Q\pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 (1-\theta) \exp\left(\frac{3\eta}{b}\right) \exp\left[-\pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 \int_0^t (1-\theta) \exp\left(\frac{3\eta}{b}\right) dt\right] \quad (10-54)$$

is obtained.

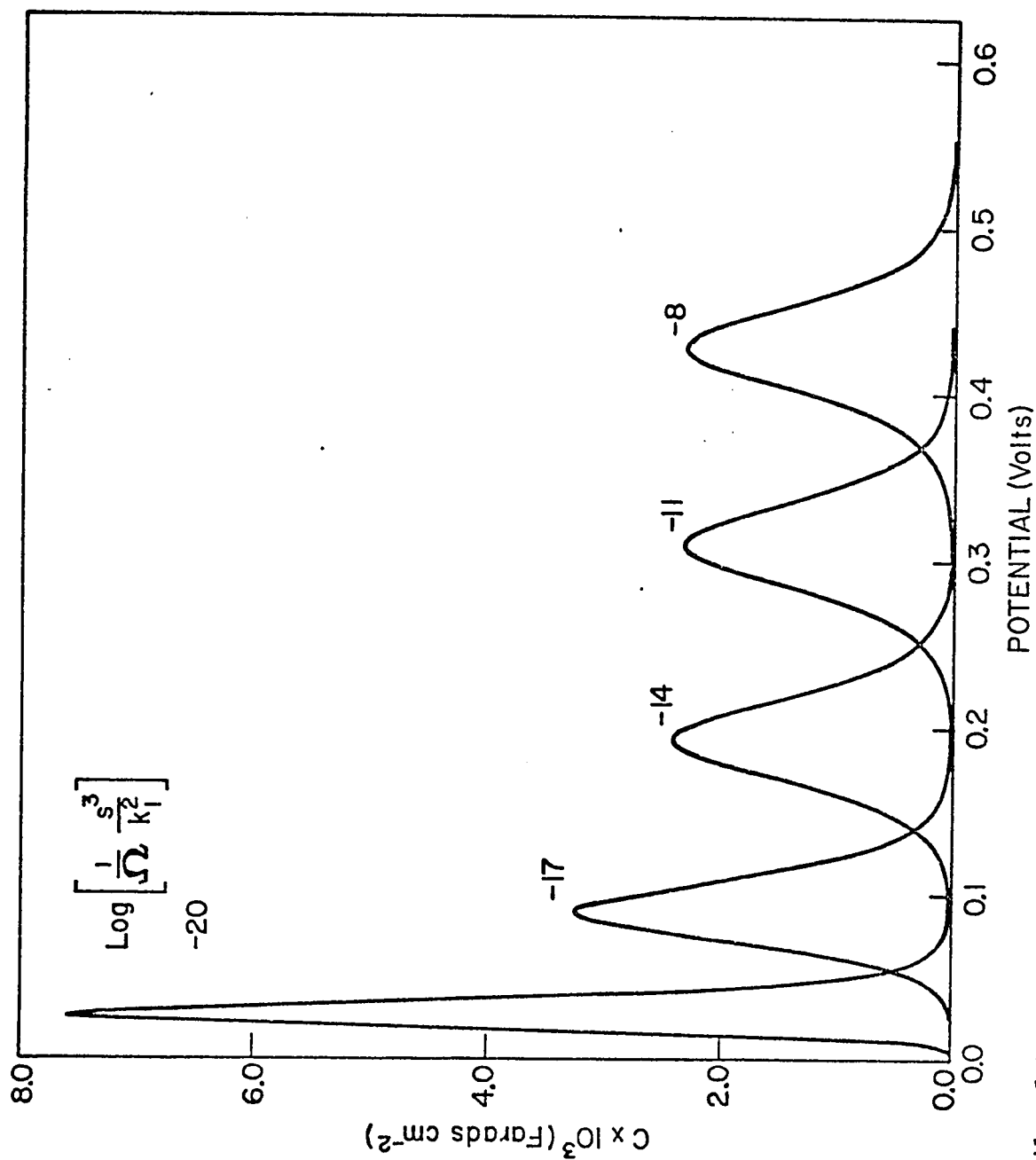


Fig. 10-6 Family of C-V profiles for a nucleation and growth process for various values of the reduced sweep-rate parameter $\frac{s_3}{\Omega k_1^2}$. In this case the density of nuclei changes with changing overpotential η as well as

10.5.2.2 Calculation of the current peak parameters

The values of V_p , θ_p and i_p can be found analytically, as in the preceding case [Case (I-2)], for reaction [2] being irreversible. Knowing that the differential form of eqn. (10-53) is

$$d\tilde{E} = \pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 (1-\theta) \exp\left(\frac{3\eta}{b}\right) dt \quad (10-55)$$

the coverage θ can be found by substituting eqn. (10-5) into (10-55), rearranging and integrating both sides, taking the boundary condition $\tilde{E} = 0$ at $t=0$; the result is

$$\theta = \frac{\frac{1}{3} \pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^3 \exp\left(\frac{3\eta}{b}\right)}{1 + \frac{1}{3} \pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^3 \exp\left(\frac{3\eta}{b}\right)} \quad (10-56)$$

By differentiating eqn. (10-56) and substituting into eqn. (10-3), the current density is obtained as

$$i = Q \frac{\pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^2 \exp\left(\frac{3\eta}{b}\right)}{\left[1 + \frac{1}{3} \pi\Omega\alpha^2 k_1^2 \left(\frac{b}{s}\right)^3 \exp\left(\frac{3\eta}{b}\right)\right]^2} \quad (10-57)$$

from which the parameters for the maximum of the function can be found in the usual way. They are

$$V_p - E_r = b \ln \frac{s}{b} - \frac{2}{3} b \ln \alpha k_1 - \frac{1}{3} b \ln \frac{\pi\Omega}{3} \quad (10-58)$$

and

$$i_p = \frac{3}{4} \frac{Qs}{b} = 0.375 \frac{QFs}{RT} \quad (10-59)$$

or

$$C_p = \frac{3}{4} \frac{Q}{b} = 0.375 \frac{QF}{RT} \quad (10-60)$$

while from eqns. (10-56) and (10-58)

$$\theta_p = 0.5 \quad (10-61)$$

The dependence of the peak parameters on reduced sweep-rate is shown in Fig. 10-7.

10.6 Growth from a Density of Nuclei which Varies as a Function of Time Only - Case (III)

10.6.1 Potentiostatic conditions - Case (III-1)

The fact that the potential is kept constant makes this case identical with the Case (II-1) (see Section 10.5.1) discussed earlier, the only difference being that now " Ω " = constant", will be potential-independent.

10.6.2 Potentiodynamic conditions - Case (III-2)

Because of the relatively large change of potential during a normal sweep experiment, a nucleation rate dependent only on time, rather than on potential, was considered unrealistic and was hence not investigated.

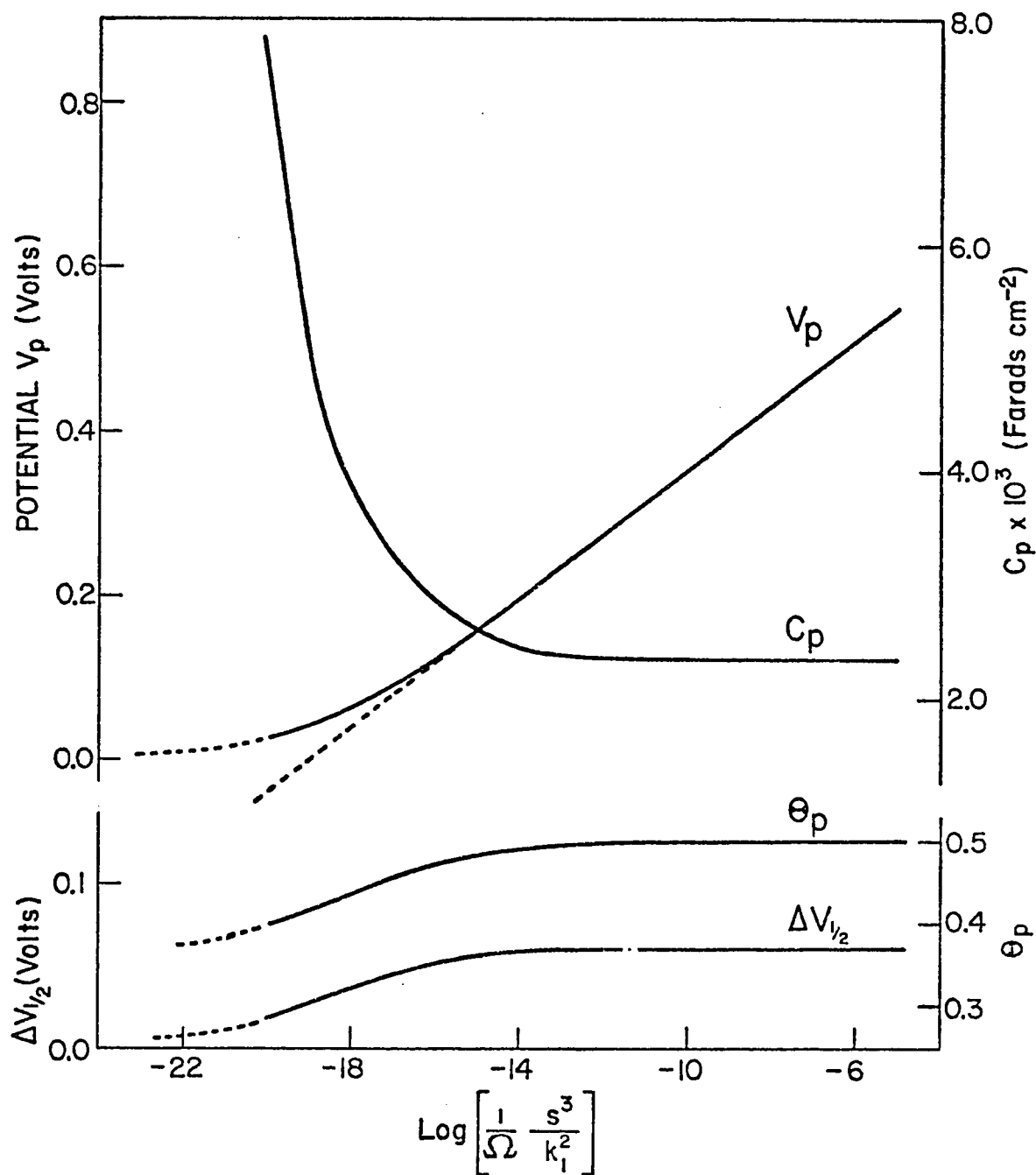


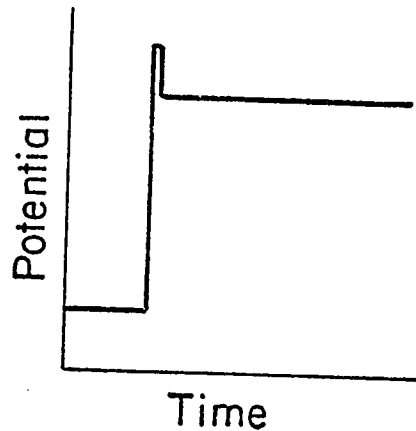
Fig. 10-7 Plots of peak parameters V_p , C_p and θ_p together with $\Delta V_{1/2}$ as a function of the reduced sweep-rate parameter $\log \frac{s^3}{\Omega k_1^2}$ for the case of varying density of nuclei with η and t , [Case (II-2)].

10.7 Growth from a Density of Nuclei which Varies as a Function of Potential and Time with Some Initially Established Density N_0 -

Case (IV)

10.7.1 Potentiostatic conditions - Case (IV-1)

For this case, the potential programme is:



and the initial conditions are:

$$\begin{aligned} \text{at} \quad t = 0 \quad N &= N_0 \\ r &= 0 \end{aligned}$$

$$\text{and} \quad V = \text{constant}$$

$$\Omega'(V) = \Omega \exp\left(\frac{V}{b}\right) = \text{constant}$$

$$v(V) = \text{constant}$$

For this case, the expectation number [eqn. (10-7)] will be the sum of the expectation numbers for Cases (I-1) and (II-1), i.e., from eqns. (10-11) and (10-39):

$$\tilde{E} = 2\pi N_0 \int_0^{r(t)} r dr + 2\pi \int_0^t \left(\int_0^{r(t)} r dr \right) j dt \quad (10-62)$$

and the current density will be the sum of current densities for Cases (I-1) [eqn. (10-13)] and (II-1) [eqns. (10-41) or (10-45)], viz.

$$i = Q[2\pi N_0 v^2 t \exp(-\pi N_0 v^2 t^2) + \frac{9\pi \Omega' v^2 t^2}{(3 + \pi \Omega' v^2 t^2)^2}] \quad (10-63)$$

Fig. 10-8 shows a comparison of i - t curves generated by the equations for growth from an initial number of nuclei $N_0 \text{ cm}^{-2}$ with continuing nucleation at a rate j . For $N_0 < 10^6 \text{ cm}^{-2}$, the i - t profile under the chosen conditions is independent of the number N_0 of any nuclei initially present, e.g., generated by a previous potential pulse; i.e., the process is controlled mainly by growth from new nuclei generated at the rate j . The dashed line in Fig. 10-8 shows the form of a potentiostatic i - t transient that would arise from a random surface process without nucleation³³. In the nucleation the i - t transients show a delay in the rise of i in comparison with that in the i - t curve for a regular surface process, as expected.

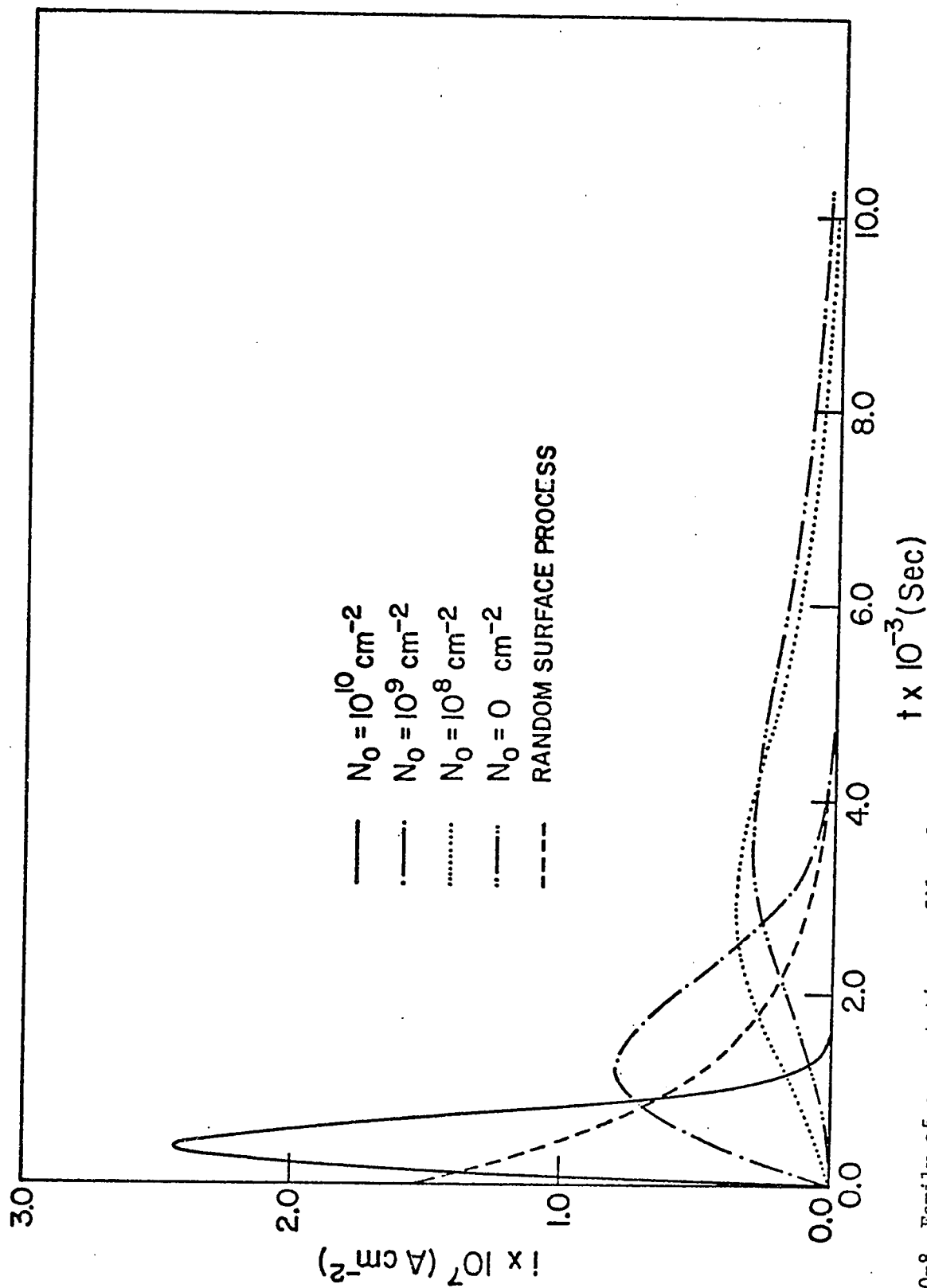
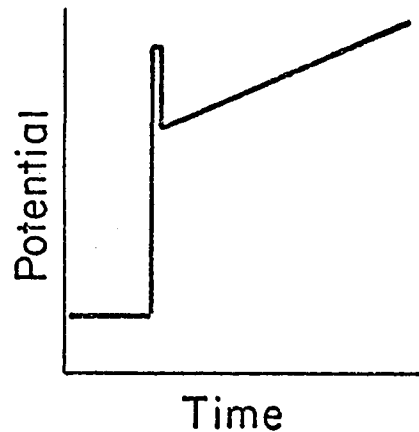


Fig. 10-8 Family of current-time profiles for a nucleation and growth process occurring from various initial densities of nuclei, N_0 , and with new nuclei appearing at a rate j determined by the rate constant $\Omega = 10^4 \text{ cm}^{-2} \text{ sec}^{-1}$. The value of $\eta = 0.1184 \text{ V}$ was chosen so that $\exp(\frac{0.1184}{b}) = 10$. For comparison, the i - t profile for a random surface process (I) is also included.

10.7.2 Potentiodynamic conditions - Case (IV-2)

The potential programme is:



and the initial conditions are:

$$\begin{aligned} \text{at } t = 0 \quad N &= N_0 \\ r &= 0 \end{aligned}$$

$$\begin{aligned} \text{and } \Delta V &= V_{in} + st - E_r = \eta \\ j &= f(V) \\ v &= f(V) \end{aligned} \tag{10-25}$$

As in the potentiostatic case, i.e., Case (IV-1), the expectation number will be the sum of the expectation numbers for Cases (I-2) [eqn. (10-27)] and (II-2) [eqn. (10-51)]:

$$\bar{E} = 2\pi N_0 \int_0^t v \left(\int_0^t v dt \right) dt + \pi \Omega \int_0^t \left(\int_0^t v dt \right)^2 (1-\theta) \exp\left(\frac{\eta}{b}\right) dt \tag{10-64}$$

and the current density the sum of the current densities for the above two cases from eqns. (10-28) and (10-52):

$$i = Q\{2\pi N_0 v \left(\int_0^t v dt\right) \exp[-2\pi N_0 \int_0^t v \left(\int_0^t v dt\right) dt] + \pi \Omega (1-\theta) \exp\left(\frac{\eta}{b}\right) \cdot \left(\int_0^t v dt\right)^2 \exp[-\pi \Omega \int_0^t (1-\theta) \exp\left(\frac{\eta}{b}\right) \left(\int_0^t v dt\right)^2 dt]\} \quad (10-65)$$

Depending on the relative values of N_0 or Ω , one term or the other in eqn. (10-65) will predominate. If the first term involving N_0 predominates, asymmetrical i - V curves arise while if the term involving Ω predominates, symmetrical curves are generated. When both terms are of comparable importance, intermediate shaped curves are observed. These effects are illustrated in Fig. 10-9.

10.8 Discussion

The characteristic features of the nucleation and growth process for the various cases presented are summarized in Table 10-1 where the corresponding potential programmes imposed on the electrode are schematically illustrated. Also the initial conditions for the calculations are listed, as well as the appropriate numbers of the key equations used in the text for the expectation number $\bar{E}$ and the current density i for each case. Finally, the values for the peak parameters V_p , i_p , C_p , t_p , $\Delta V_{1/2}$ and θ_p are also tabulated.

10.8.1 Behaviour under potentiostatic conditions

As was shown for constant-potential conditions, the current density for formation of a monolayer by the nucleation and growth mechanism [Cases (I-1), (II-1) and (III-1)] goes through a maximum.

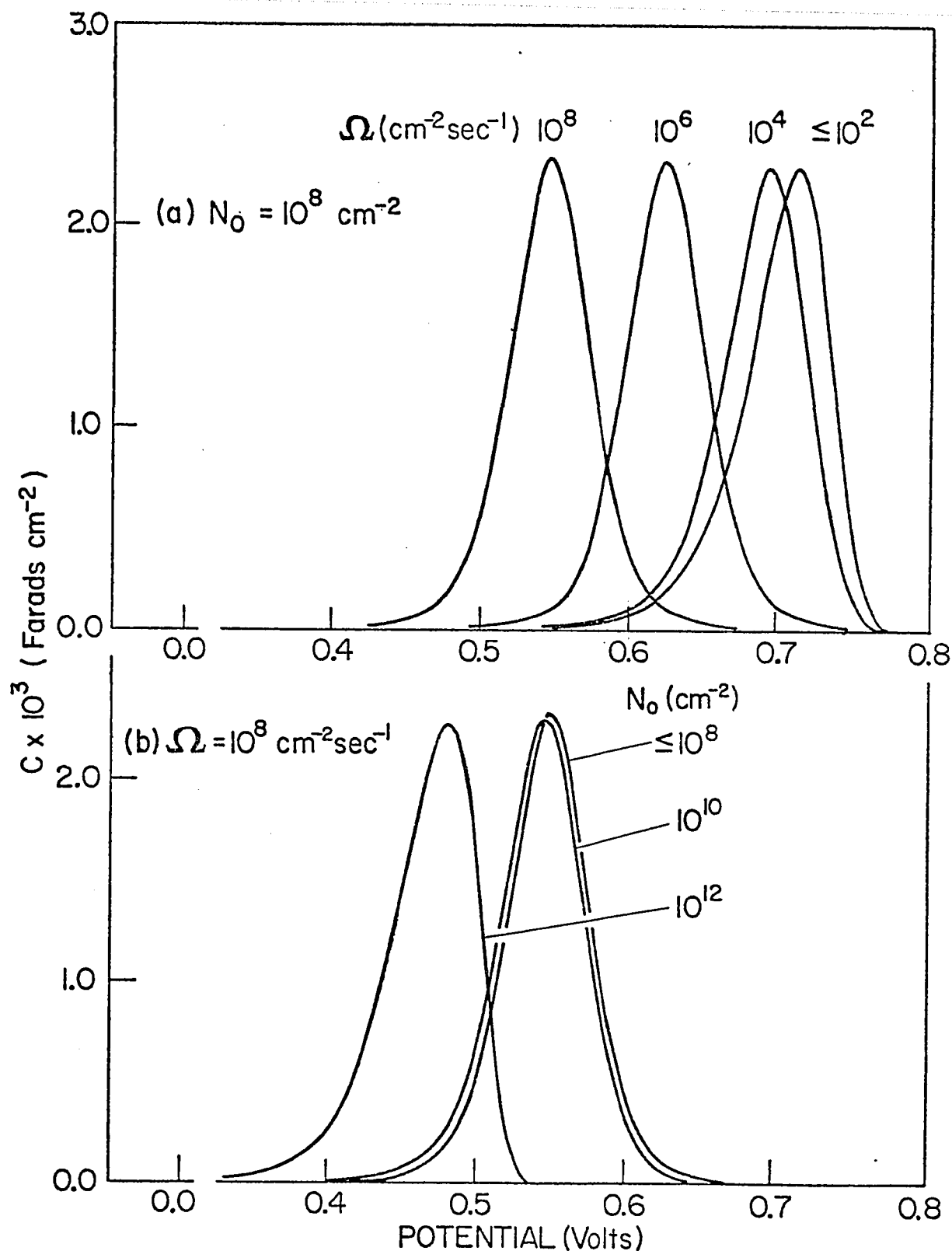
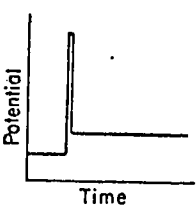
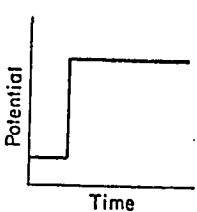
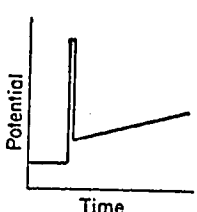
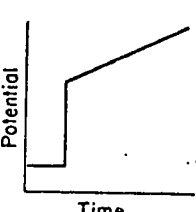


Fig. 10-9 Families of C-V profiles for the general case of a nucleation and growth process where growth occurs from an initial density of nuclei, N_0 , and from more nuclei generated in time at a rate characterized by Ω .
 (a) For $N_0 = 10^8 \text{ cm}^{-2}$ with $\Omega = 10^8, 10^6, 10^4, \leq 10^2 \text{ cm}^{-2} \text{ sec}^{-1}$.
 (b) For $\Omega = 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ with $N_0 = 10^{12}, 10^{10}, \leq 10^8 \text{ cm}^{-2}$.
 Sweep-rate $s = 1.0 \text{ V sec}^{-1}$ for both cases.

Table 10-1: Conditions and Characteristic Parameters for the Kinetic Behaviour of a Nucleation and Growth Mechanism of Monolayer Growth under Potentiostatic and Potentiodynamic Control

ITEM	POTENTIOSTATIC CASES ($V = \text{constant}$)		POTENTIODYNAMIC CASES ($\frac{dV}{dt} = \text{constant}$)	
	Case (I-1)	Cases (II-1) and (III-1)	Case (I-2)	Case (II-2)
Potential Programme				
Initial conditions	$N = N_0$ $r = 0$ $\Omega = 0$ $v(V) = \text{constant}$	$N = 0$ $r = 0$ $\Omega'(V) = \text{constant}$ $v(V) = \text{constant}$	$N = N_0$ $r = 0$ $\Omega = 0$ $v = f(V)$	$N = 0$ $r = 0$ $\Omega' = f(V)$ $v = f(V)$
Equations used for: $\tilde{E}$ i	(10-12) (10-13)	(10-40) (10-41), (10-45)	(10-27) (10-28)	(10-51) (10-52)
Current peak parameters				
$V_p - E_r$	-	-	$b \ln \frac{s}{b} - b \ln \alpha k_1$ $- \frac{1}{2} b \ln \pi N_0$	$b \ln \frac{s}{b}$ $- \frac{2}{3} b \ln \alpha k_1$ $- \frac{1}{3} b \ln \frac{\pi \Omega}{3}$
θ_p	0.394	$\frac{1}{3}$	0.632	0.5
C_p	-	-	$0.368 \frac{QF}{RT}$	$0.375 \frac{QF}{RT}$
i_p	$0.607 \frac{Q}{t_p}$	$\frac{2}{3} \frac{Q}{t_p}$	$0.368 \frac{QFs}{RT}$	$0.375 \frac{QFs}{RT}$
t_p	$\left(\frac{1}{2\pi N_0 v^2}\right)^{1/2}$	$\left(\frac{3}{2\pi \Omega' v^2}\right)^{1/3}$	-	-
$i_p t_p$	$0.607 Q$	$\frac{2}{3} Q$	-	-
$\Delta V_{1/2}$	-	-	0.063 Volts	0.060 Volts

The peak current of the asymmetrical profile observed on i - t plots (Figs. 10-2 and 10-5) is inversely proportional to the time t_p at which it occurs [see eqns. (10-18) and (10-49)]. The presence of this characteristic peak makes it possible to distinguish a mechanism of nucleation and growth from one of random deposition in monolayer formation (or desorption in monolayer stripping) in which, at constant potential, the current density will decrease continuously with time, (Fig. 10-10), due to the effect of diminishing free surface $(1-\theta)$.

As can be seen from Table 10-1 and Figs. 10-2, 10-5, the shapes of i - t peaks for the two potentiostatic cases [(I-1) and (II-1)] differ very little (for these calculations, the values of N_0 and Ω were chosen so that the number of nuclei on the surface growing during monolayer formation was of the same order in both cases). For the Case (II-1), with the number of nuclei increasing with time and potential, the peaks are, as expected, higher and narrower, and occur earlier than for the case where growth arises from a constant number of nuclei N_0 [Case (I-1)], but the differences dependent on N_0 and Ω are not large enough to be of diagnostic value. Also the values of θ_p and the product $i_p t_p$ which are independent of N_0 and the kinetic parameters, do not differ enough to be used as criteria for identifying cases [see Table 10-1; eqns. (10-20), (10-50) and (10-18), (10-49)]. The principal feature which distinguishes the two cases is the more rounded shape of the peak with a shorter foot for Case (I-1), and the more concave form of the flanks of the peak for Case (II-1) together with a relatively long tailing of the current (see Figs. 10-2 and 10-5).

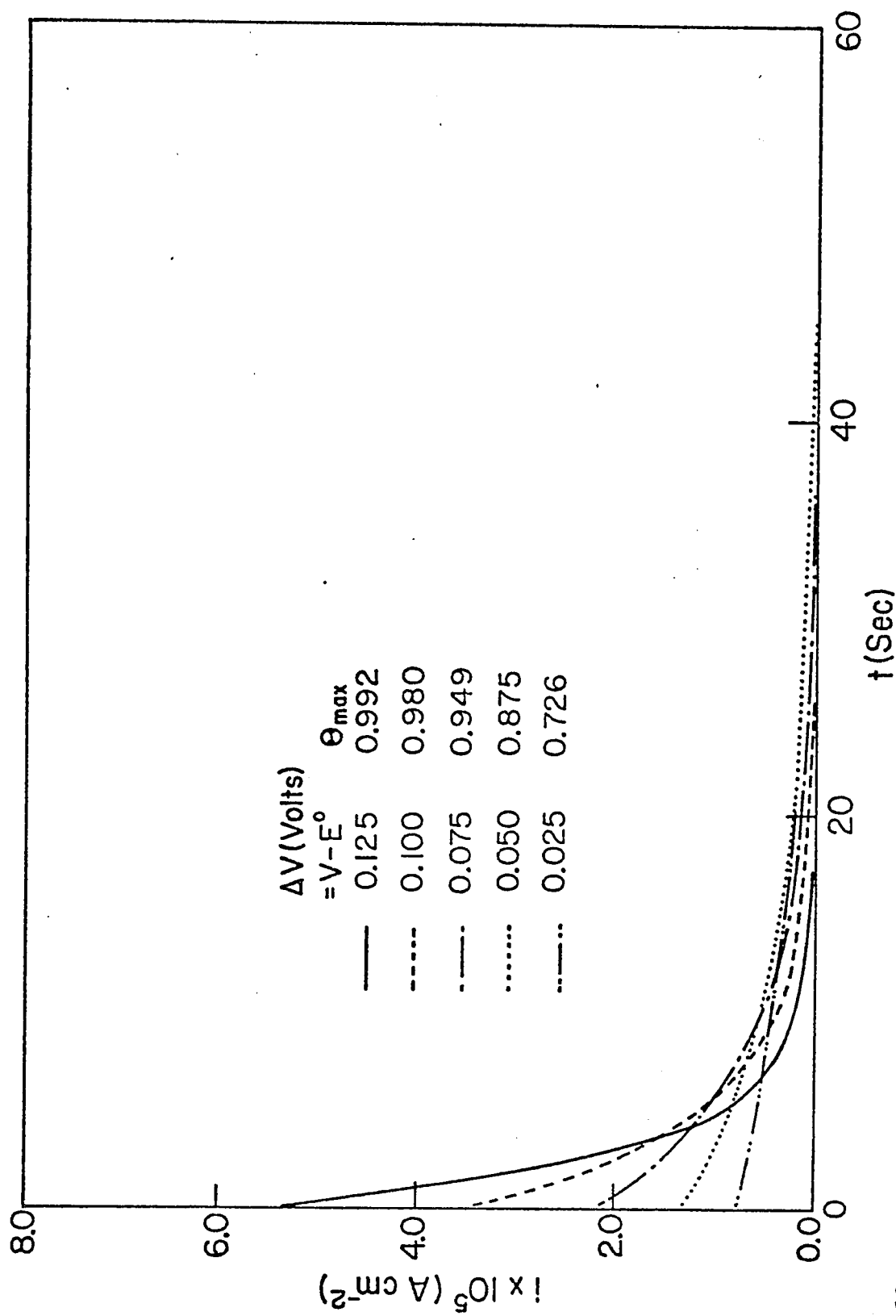


Fig. 10-10 Plots of i - t profiles for a reversible random surface process [reaction (I) Langmuir conditions] for voltage pulses of $\Delta V = 0.025, 0.050, 0.075, 0.100$ and 0.125 V. The corresponding maximum coverages, $\theta_{\max}$, which are realized with the values of ΔV are also indicated.

$k_1 = k_{-1} = 3.162 \times 10^{-2} \text{ sec}^{-1}$, $E^\circ = 0.0$ V.

10.8.1.1 The kinetic parameters of the process

The dependence of i_p on overvoltage η - the measure of the irreversibility of the growth process - is shown in Fig. 10-11. For the two cases considered, a relation of the Tafel type (cf. ref. 33 and Chapter IV for the behaviour of the l-e surface process) is obtained, giving for irreversible conditions in reaction [2] a straight line having a slope $\frac{1}{2.3b}$. Although the intercept of these lines at $\eta = 0$ will not lead to the individual kinetic parameters for the nucleation reaction [1] and for the growth process [2], it can yield a compound kinetic parameter which is usefully characteristic of the overall process (IX).

For growth from a constant number of nuclei [Case (I-1)] under irreversible conditions, the value of the time t_p for the peak current to be attained may be derived from eqns. (10-8) and (10-16) as

$$t_p = \left[\frac{1}{2\pi N_o \alpha^2 k_1^2 \exp(\frac{2\eta}{b})} \right]^{1/2} \quad (10-66)$$

or

$$t_p = 0.399 \exp(-\frac{\eta}{b}) \left(\frac{1}{N_o \alpha^2 k_1^2} \right)^{1/2} \quad (10-67)$$

which with eqn. (10-17) gives for the peak current density

$$i_p = 1.519 Q \exp(\frac{\eta}{b}) (N_o \alpha^2 k_1^2)^{1/2} \quad (10-68)$$

and for the intercept in Fig. 10-11a at $\eta = 0$

$$\log i_{p,o} = \log [1.519 Q (N_o \alpha^2 k_1^2)^{1/2}] \quad (10-69)$$

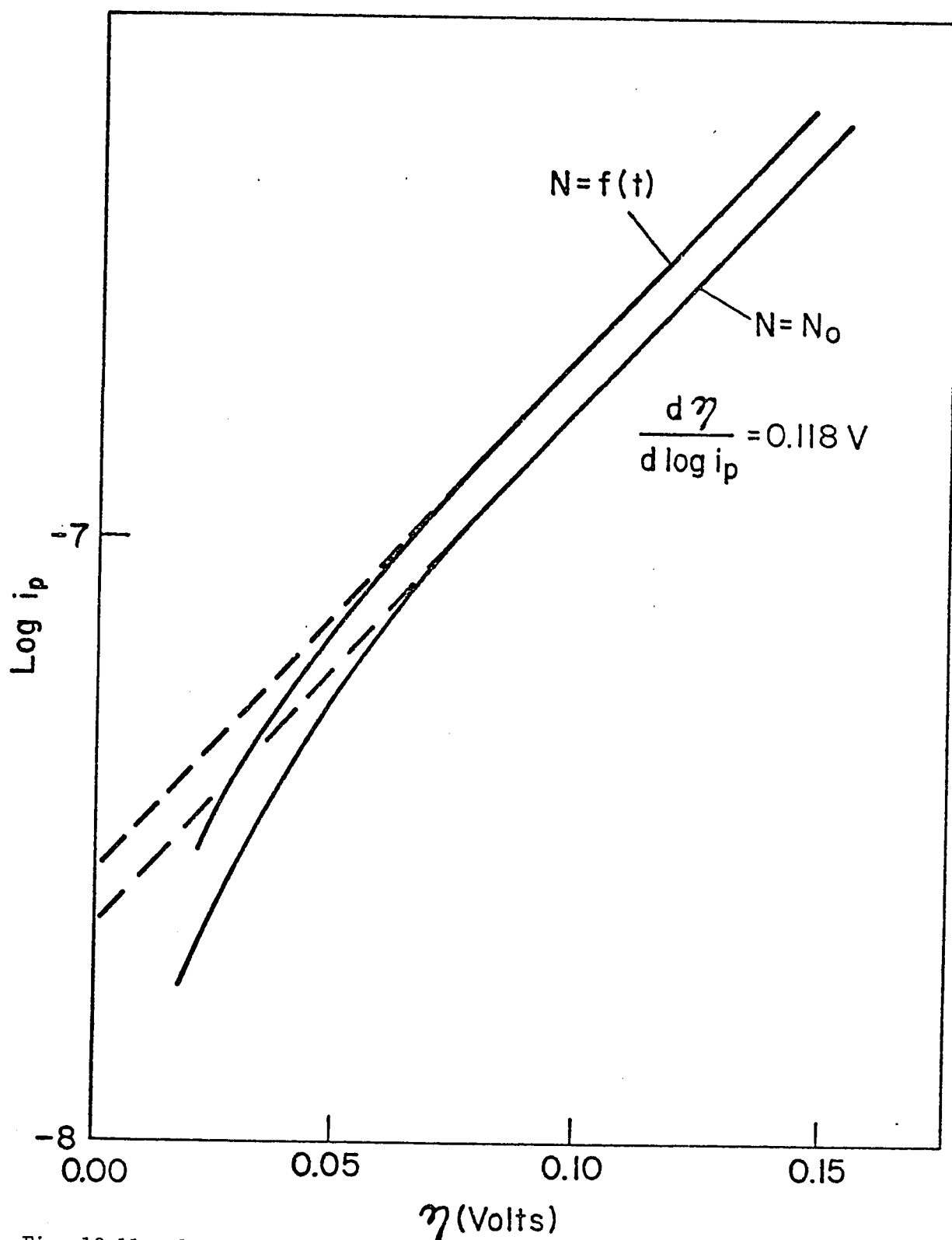


Fig. 10-11 Plot of $\log i_p$ vs. η for potentiostatic conditions corresponding to:

- (a) Constant density of nuclei initially present ($N_0 = 10^{10} \text{ cm}^{-2}$), [Case (I-1)].
- (b) Density of nuclei varying with time at a rate characterized by the rate constant $\Omega = 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$, [Case (II-1)].

For Case (II-1) eqns. (10-8), (10-47) and (10-48) will give for the intercept (see Fig. 10-11b)

$$\log i_{p,o} = \log\left[\frac{2}{3}\left(\frac{2\pi}{3}\right)^{1/3} Q(\Omega\alpha^2 k_1^2)^{1/3}\right] \equiv \log[0.853 Q(\Omega\alpha^2 k_1^2)^{1/3}] \quad (10-70)$$

Similar graphs can be plotted for the dependence of t_p on η , with a resulting slope of $-\frac{1}{2.3b}$ and intercepts for Case (I-1) as

$$\log t_{p,o} = -\log[(2\pi)^{1/2} (N_o\alpha^2 k_1^2)^{1/2}] \equiv -\log[2.507 (N_o\alpha^2 k_1^2)^{1/2}] \quad (10-71)$$

and for Case (II-1) as

$$\log t_{p,o} = -\log\left[\left(\frac{2\pi}{3}\right)^{1/3} (\Omega\alpha^2 k_1^2)^{1/3}\right] \equiv -\log[1.279(\Omega\alpha^2 k_1^2)^{1/3}] \quad (10-72)$$

The kinetics of the process depend, as is seen here, on the parameters $N_o\alpha^2 k_1^2$ and $\Omega\alpha^2 k_1^2$, the same as those which determine the irreversibility of the reaction in potentiodynamic experiments.

It is to be noted that $\log t_p - \eta$ graphs are especially useful because they do not involve any experimental data which have to be related to the real surface area of the electrode.

10.8.1.2 Reduced current density versus reduced time plots

It is always desirable to be able to express the kinetic behaviour of a process in a general way that is independent of the numerical values of the parameters involved. This is possible for the two Cases (I-1) and (II-1) considered. A unique current density - time curve which is independent of the values of kinetic parameters involved can be constructed by plotting reduced current i/i_p vs. the reduced time t/t_p .

When growth occurs from a constant density of nuclei [Case (I-1)] the equation for the reduced values of current density as a function of time can be obtained by substituting eqns. (10-16) and (10-17) into eqn. (10-13); then

$$\frac{i}{i_p} = \frac{t}{t_p} \exp\left\{\frac{1}{2}\left[1 - \left(\frac{t}{t_p}\right)^2\right]\right\} \quad (10-73)$$

is obtained.

Similarly, for the case where growth occurs from a density of nuclei which varies with time at a given potential [Case (II-1)], the relation between reduced current density and reduced time is derived by substituting eqns. (10-47) and (10-48) into eqn. (10-45) and gives

$$\frac{i}{i_p} = \frac{9\left(\frac{t}{t_p}\right)^2}{\left[2 + \left(\frac{t}{t_p}\right)^3\right]^2} \quad (10-74)$$

Also, common reduced curves of θ vs. t/t_p will arise for the two cases. Thus from eqns. (10-16) and (10-19)

$$\theta = 1 - \exp\left[-\frac{1}{2}\left(\frac{t}{t_p}\right)^2\right] \quad (10-75)$$

for Case (I-1) and from eqns. (10-44) and (10-47)

$$\theta = \frac{\left(\frac{t}{t_p}\right)^3}{2 + \left(\frac{t}{t_p}\right)^3} \quad (10-76)$$

for Case (II-1).

These equations show that for a given value of t/t_p ratio only one value of θ and i/i_p results, respectively, for each case considered.

A convenient diagnostic criterion for distinguishing the two cases in terms of their kinetic behaviour is to calculate the values of the reduced currents at half the peak time t_p . For Case (I-1) $\frac{i}{i_p} = 0.73$ while for Case (II-1) $\frac{i}{i_p} = 0.5$ at that point.

10.8.2 Behaviour under potentiodynamic conditions: Characteristics of the i - V profiles for a nucleation and growth process

The dependence of the peak parameters V_p , C_p , θ_p and the peak half-width $\Delta V_{1/2}$ on the reduced sweep-rate was shown in Figs. 10-4 and 10-7.

The overall picture is the same for both cases, i.e., the growth from constant number of nuclei N_0 and from a potential-dependent number of nuclei: the parameters C_p , θ_p and $\Delta V_{1/2}$ have respective constant characteristic values only for a totally irreversible growth process. With increasing reversibility, the C_p will increase (theoretically to infinity) while θ_p and $\Delta V_{1/2}$ will decrease, i.e., the peak will become higher and narrower approaching a pulse of current limitingly under reversible conditions. Hence there is no characteristic profile for reversible conditions (in practice, other processes will then control the growth).

For both cases, viz. when N is constant or is $f(V)$, V_p shifts 0.118 V for every decade change of s when the process is driven to

irreversible behaviour, as can be seen from Figs. 10-3, 10-4, 10-6 and 10-7 as well as from eqns. (10-34) and (10-58).

The intercept of the plot of V_p vs. $\log s$ at $V_p - E_r = 0$ gives an "overall" rate constant of the process, the same as in the potentiostatic case. The intercept for the Case (I-2) is given from eqn. (10-34) by

$$\ln s_o = \ln[b\alpha k_1 (\pi N_o)^{1/2}] \quad (10-77)$$

and for the Case (II-2), from eqn. (10-58), by

$$\ln s_o = \ln[b(\alpha k_1)^{2/3} (\frac{\pi}{3} \Omega)^{1/3}] \quad (10-78)$$

where b , π and α are constants. Therefore the kinetics of the process will depend on $N_o^{1/2} k_1^{2/2}$ in the first case and on $\Omega^{1/3} k_1^{2/3}$ in the second. These products correspond to the overall rate constants for the processes.

The reduced sweep-rate, which is the measure of irreversibility in a reaction studied by the potentiodynamic method, is the ratio of the sweep-rate s to the rate constant of the process in the case of a simple surface process³³. For more complex processes, as e.g. nucleation and growth considered here, the reduced sweep-rate characterizing the kinetics of the overall process will evidently be the product of all the ratios:

$$\frac{s}{b \times \text{rate-constant}}$$

which will be $\frac{s}{b\Omega}$ for nucleation and $\frac{s}{bk_1}$ for the process of growth while for the growth of the perimeters of the circles it will again be $\frac{s}{bk_1}$. Hence the reduced sweep-rate for the overall process will be $\frac{s^3}{b^3\Omega k_1^2}$.

The following interesting comparison can then be made between the expressions for $\ln s_o$ in terms of rate-constant parameters for various surface processes:

- (i) for 1-e random surface reaction (see Chapter IV and also ref. 33) (one rate process):

$$\ln s_o = \frac{1}{1} \ln(bk_1) \quad (10-79)$$

- (ii) for nucleation and circle growth with a fixed number of nuclei (two rate processes; deposition in the growth step and time-dependence of circle radii):

$$\ln s_o = \frac{1}{2} \ln(b^2 \alpha^2 k_1^2 \pi N_o) \quad (10-77)$$

and

- (iii) for nucleation and circle growth with a potential-dependent density of nuclei (three rate processes):

$$\ln s_o = \frac{1}{3} \ln(b^3 \alpha^2 k_1^2 \Omega \frac{\pi}{3}) \quad (10-78)$$

It is to be observed that the magnitude of $\ln s_o$, and hence the reversibility of the surface process, is determined not only by the rate constant k_1 but by its product with other system-dependent parameters such as α , N_o and Ω .

The relative shapes of the C-V curves for a fixed [Case (I-2)] and potential-dependent [Case (II-2)] nucleation density are compared in Fig. 10-12 where a C-V peak for the random l-e surface process is also shown for comparison. The profiles have been set on the potential axis so that the peak potentials are at an arbitrary common value on a relative potential scale. The extents of asymmetry and the $\Delta V_{1/2}$ values are to be noted.

The parameter most useful for distinguishing between Cases (I-2) and (II-2) is θ_p , the coverage to the peak under conditions of irreversible growth. For growth from a constant number of nuclei [Case (I-2)], the peak is asymmetrical with $\theta_p = 0.63$ [Table 10-1, eqn. (10-35)] in contrast to the value $\theta_p = 0.50$ for the symmetrical peak which arises when growth occurs from a potential-dependent surface density of nuclei, eqn. (10-61).

10.8.3 Criteria for distinguishing nucleation-controlled processes from random deposition in monolayer formation

The first and experimentally easiest characteristic to evaluate which is different for the two mechanisms of monolayer formation is that in contrast to random deposition, the nucleation-controlled process does not give a unique, constant peak for reversible conditions.

Secondly, it is useful to compare the shape of the irreversible i-V profiles for nucleation-controlled growth of a monolayer with that for the same electrochemical surface reaction proceeding at random^{33,90}, i.e., with a rate determined by $1-\theta$, as well as by $\exp(\pm \frac{\Delta V}{b})$ and the

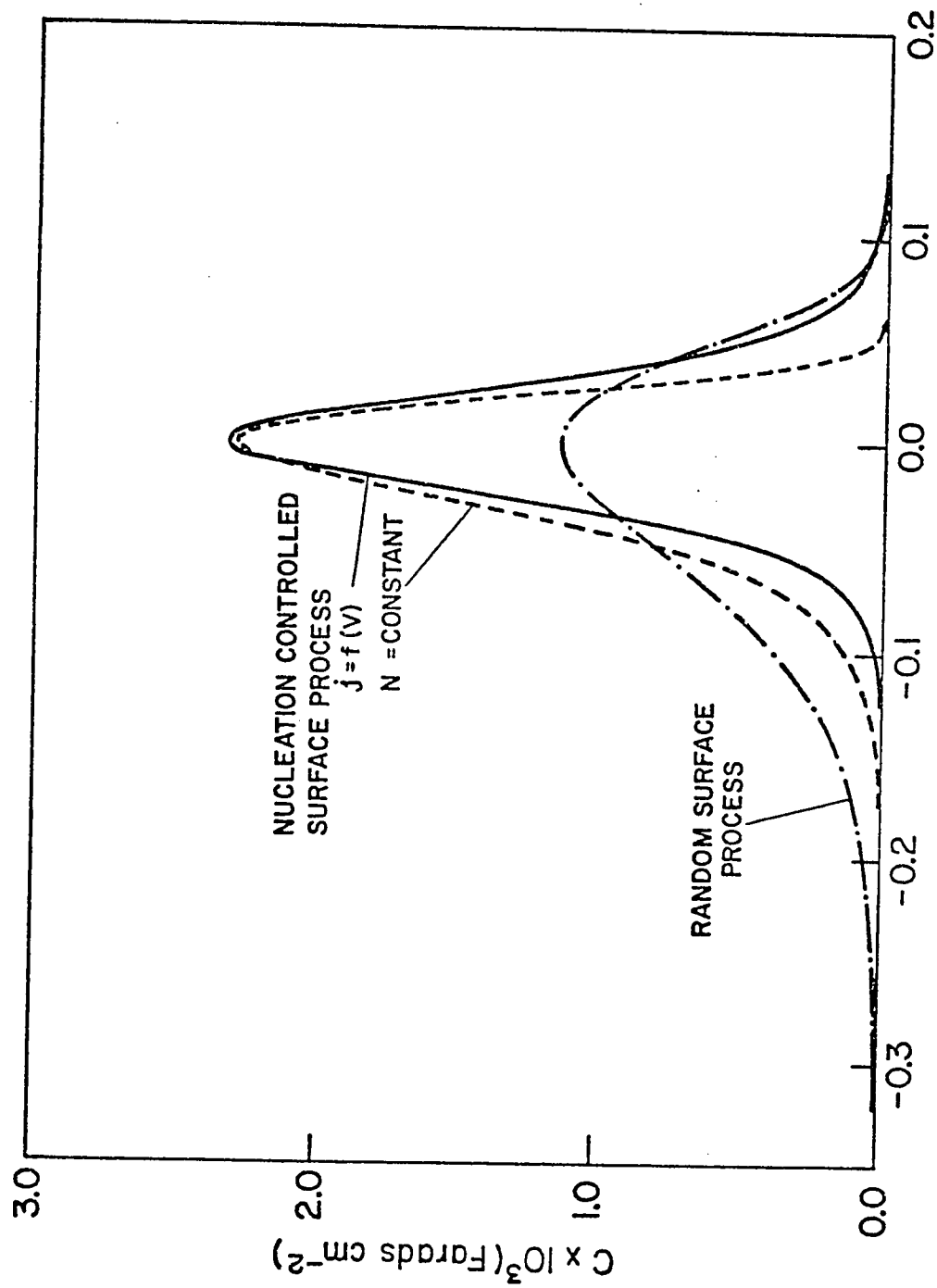


Fig. 10-12 Comparison of the shapes of nucleation-controlled irreversible C-V profiles with that for a random deposition process (I) (Langmuir case, $g = 0$). (Peak potentials have been normalized to a common value of 0.0 V to facilitate comparison of the shapes of the curves.)

rate constant. Fig. 10-12 shows such a comparison for the current peaks generated by a totally irreversible process for the indicated values of the parameters in a typical case for $N = N_0$, $j = 0$ and $j = f(V)$ with initial number of nuclei $N = 0$. The C-V profile for the random deposition case (1-e irreversible Langmuir surface process) is calculated as shown previously (see Chapter IV and ref. 90).

The interesting feature of Fig. 10-12 is that the current peak for the nucleation case is much sharper than that for the random deposition case. This is again because the surface process is, in a sense, delayed with respect to changing time and potential by the restriction imposed by growth at the perimeters of expanding circles; however, it is in a sense also "autocatalytic" since in the initial stages, the more the circles grow (until they overlap), the greater is the number of perimeter sites at which the electrochemical process can occur. In the random case, the electrochemical process depends simply on $1-\theta$, the total free area, at any potential. The peak is consequently sharper in the nucleation case, the half-width⁹³ being only about 60 mV instead of 126 mV.

For the Case (I-2), C_p is twice as large as its value for random deposition under conditions of Langmuir adsorption (see Chapter IV and ref. 90), θ_p is the same and $\Delta V_{1/2}$ is half. For the Case (II-2), C_p and $\Delta V_{1/2}$ are also nearly twice as large and small, respectively, but θ_p is different - equal to 0.5, indicating a symmetrical C-V profile.

A comparison of the characteristic features of an irreversible random deposition process with those of nucleation and growth is given in Table 10-2.

It is seen that although C_p and $\Delta V_{1/2}$ for nucleation-controlled and random deposition processes with high attractive interactions, i.e., negative values of g , in the deposited adsorbed layer are similar, the symmetry of the peaks is different as indicated by θ_p .

Table 10-2 Characteristic Values of C_p , θ_p and $\Delta V_{1/2}$ for Nucleation-Controlled and Random Deposition of a Monolayer

Mechanism	Irreversible random process			Nucleation and growth	
Parameter \ g	0	-3.8	-4	$N=N_0$	$N=f(V)$
$C_p \times 10^3$ (Farads cm^{-2})	1.15	2.00	2.15	2.30	2.34
$\Delta V_{1/2}$ (Volts)	0.126	0.063	0.060	0.063	0.060
θ_p	0.63	0.71	0.72	0.63	0.50

Thirdly, an interesting characteristic behaviour arises if the potential is stepped to a certain value before the potential sweep is applied, as shown in Figs. 10-13 and 10-14. The C-V response is shown in the families of curves of Fig. 10-13 for constant nucleation density N_0 , and in Fig. 10-14 for a potential-dependent nucleation rate j according to eqn. (10-1).

In each case in Figs. 10-13 and 10-14, the current ascends to a peak and descends and the peak potential moves progressively with increasing the initial potential V_{in} to which the applied voltage was

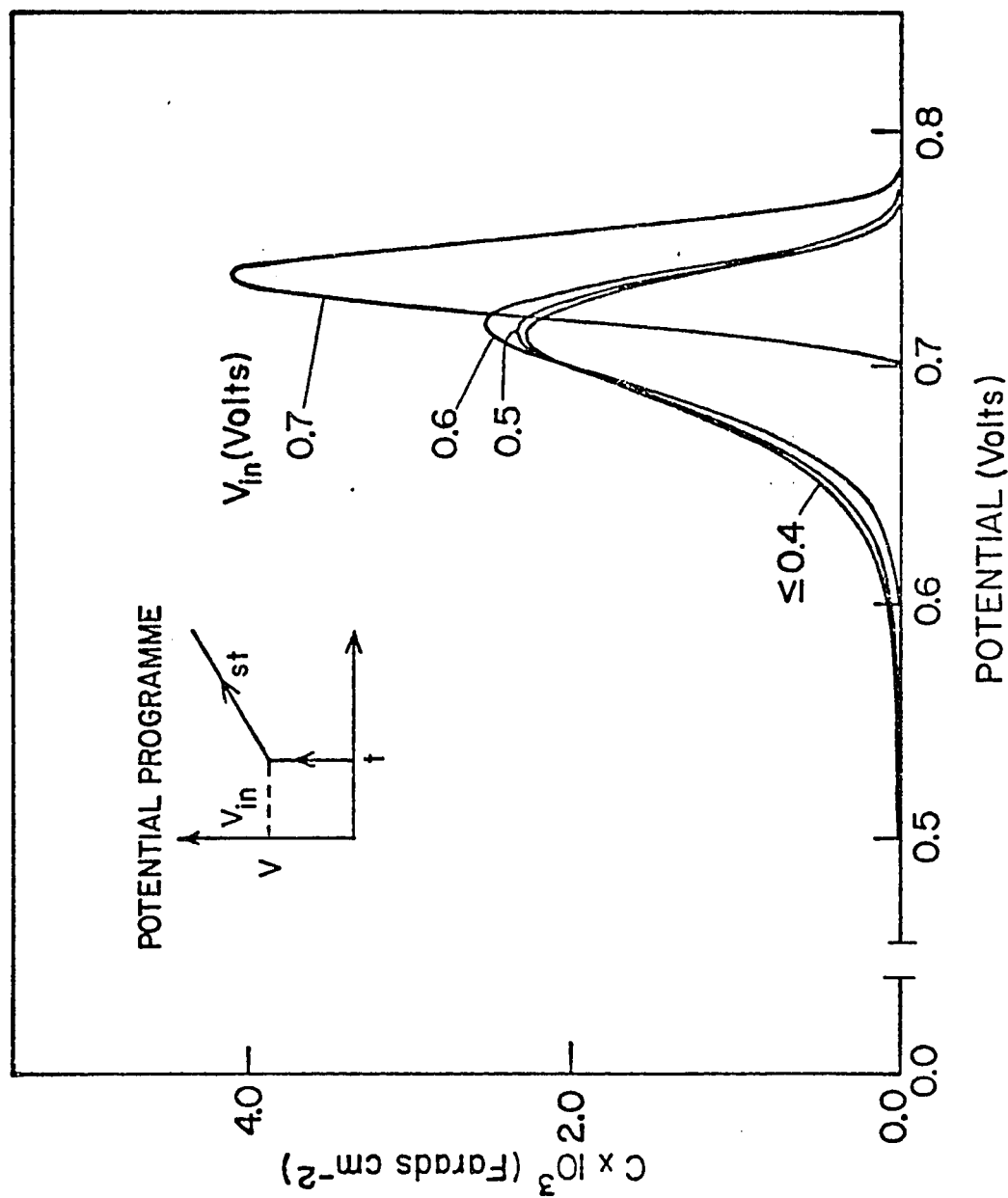


Fig. 10-13 Families of C-V profiles for a nucleation and growth process resulting from stepping the potential from E_r to various initial potentials V_{in} , followed by application of a linear potential sweep. A constant density of nuclei $N_0 = 10^8 \text{ cm}^{-2}$ is taken and the value of the reduced sweep-rate parameter $\frac{1}{N_0} \left(\frac{s}{k_1} \right)^2 = 10^{-5} \text{ V}^2 \text{ cm}^2$ for $s = 1.0 \text{ V sec}^{-1}$.

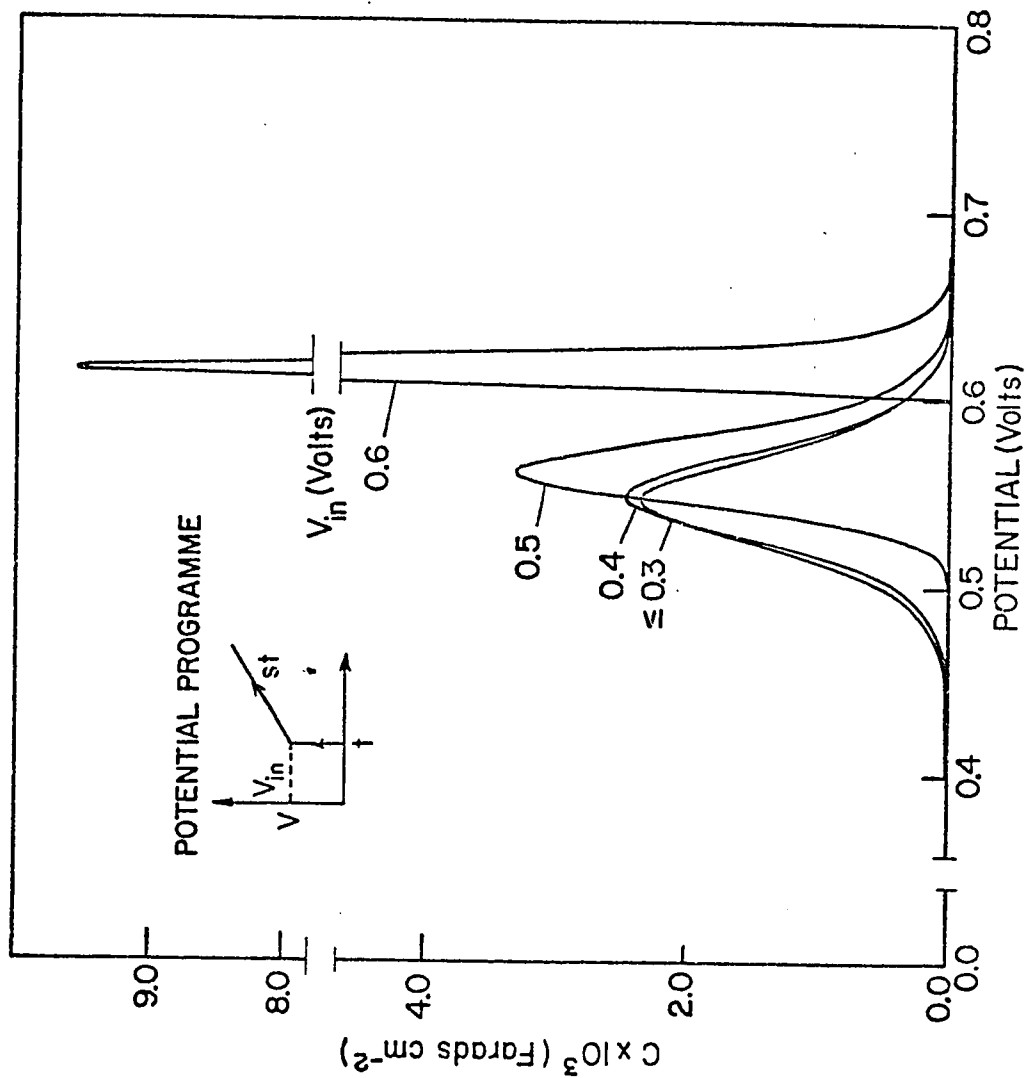


Fig. 10-14

Series of C-V profiles for a nucleation and growth process resulting from stepping the potential from E_r to various values of the initial potential V_{in} , followed by application of a linear potential sweep. A constant nucleation rate characterized by $\Omega = 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ is taken and the value of the reduced sweep-rate parameter $\frac{s^3}{\Omega k_1} = 10^{-5} \text{ V}^3 \text{ cm}^2$ for $s = 1.0 \text{ V sec}^{-1}$.

stepped. The peaks in Fig. 10-13 ($j = 0$) are all more asymmetric than the representative ones of Fig. 10-14 for $j = f(V)$ and $N_0 = 0$. In the case of the random surface process not requiring nucleation, the results (Fig. 10-15) of applying the potential programme, shown in Fig. 10-15 as well is to establish the maximum current density which can be passed at potential V_{in} on a completely free surface ($1-\theta = 1$). The current density is larger than would be the case if the sweep had been initiated from a lower potential and a certain coverage had been built up on the surface; the current peaks are correspondingly higher. Unlike the profiles of Figs. 10-13 and 10-14, the peak currents arise at the same peak potentials. If the initial potential V_{in} is, however, stepped higher than the normal peak potential, only part of the curve will be registered and all of the charge is passed beyond the normal peak of the curve (curve 5 of Fig. 10-15).

The qualitatively different response of the random and nucleation-controlled process in Figs. 10-13 and 10-14 compared with Fig. 10-15, thus provides a useful diagnostic criterion for the two types of surface processes.

Finally, the effect of reversing the sweep before the current peak is completed (i.e., for $i < i_p$) gives a clear basis for distinguishing a nucleation-controlled process from the random one. In the case of a nucleation-controlled surface process, reversal of the sweep before the growing circles overlap produces a continuing increase of current since growth around existing nuclei continues along longer perimeters in the reversed sweep and also nuclei continue to be formed for the case of

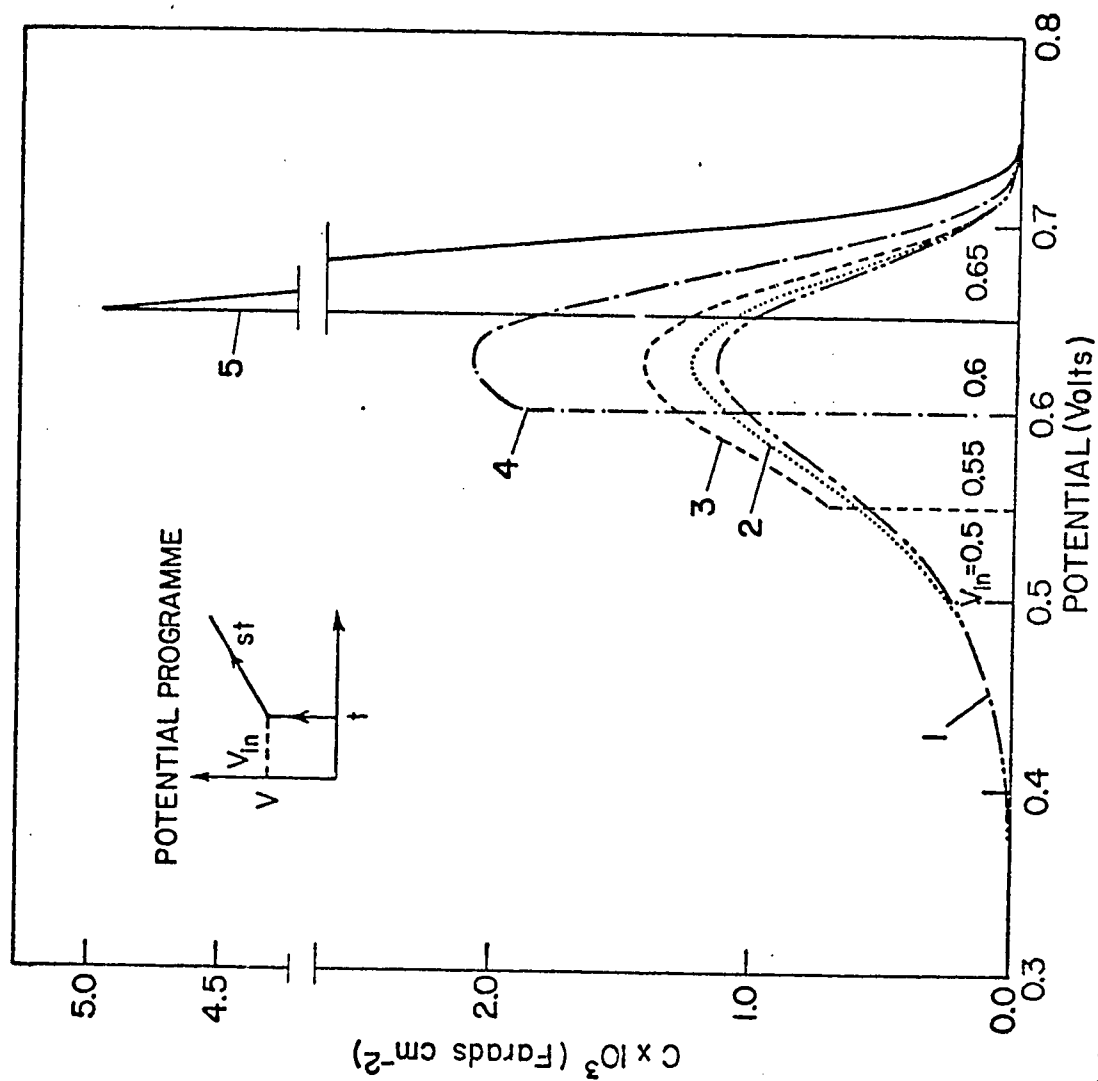


Fig. 10-15 Families of C-V profiles for an irreversible random deposition surface process (I) (Langmuir conditions, $g = 0$) resulting from stepping the potential to various values of V_{in} followed by application of a linear potential sweep for $\frac{s}{k} = 10^4$ V and $F^\circ = 0.0$ V.

$j \neq 0$. This is because in a nucleation-controlled process, the electrochemical process of growth is normally proceeding under irreversible conditions. The results of calculations on sweep reversal at various potentials in the sweep are shown in Figs. 10-16a,b for constant initial number of nuclei ($j=0$) and for $j = f(V)$. A characteristic feature of Figs. 10-16a,b is that the i - V curves, after reversal of the sweep, always lie above the i - V profile for the forward direction of the sweep if sweep reversal is made before the current peak is reached.

For random deposition processes at a surface, as was shown previously³³, reversal of the direction of a sweep will immediately produce in the reversible case, currents of opposite sign but of the same magnitude. For irreversible behaviour, the current in the reversed sweep will initially have the same sign³³ but due to the progressively decreasing free surface the current will always be smaller than that on the forward direction of the sweep at the same potential (see also Chapter IV).

10.9 Conclusions

Simulation of the kinetic behaviour of monolayer formation by a nucleation and growth mechanism for different cases shows that for both potentiostatic and potentiodynamic conditions there are several useful characteristic features which distinguish this type of process from the one in which monolayer formation occurs by random deposition under Langmuir adsorption conditions.

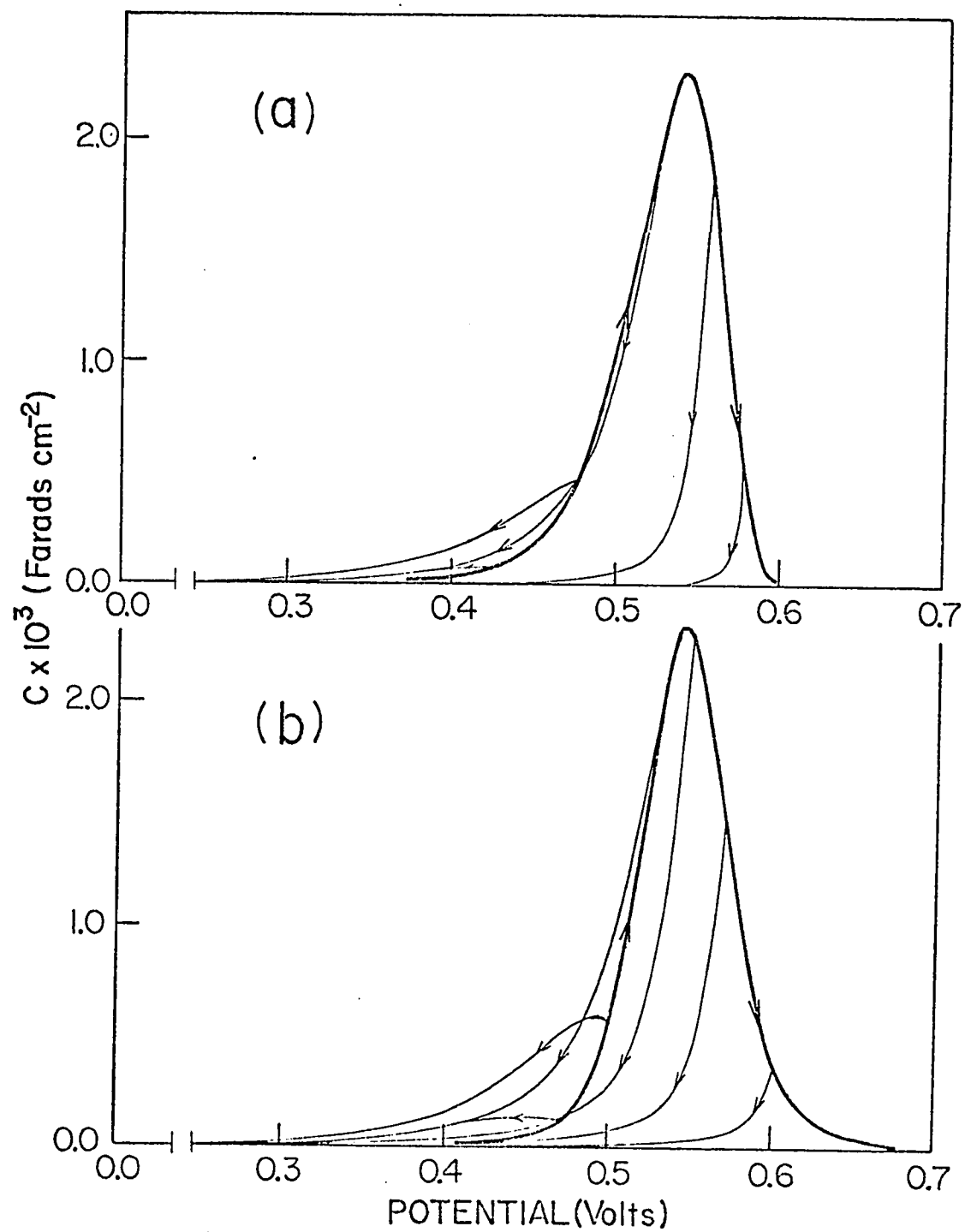
Fig. 10-16 Behaviour of the C-V profiles for a nucleation and growth process when the sweep is reversed at various potentials in the anodic direction of sweep: $s = 1.0 \text{ V sec}^{-1}$:

- (a) For the case when a constant number

$$N_0 = 7.096 \times 10^{10} \text{ cm}^{-2} \text{ of nuclei is present. Reduced sweep-rate parameter } \frac{1}{N_0} \left(\frac{s}{k_1} \right)^2 = 1.409 \times 10^{-8} \text{ V}^2 \text{ cm}^2.$$

- (b) As in (a) but for a constant rate of nucleation characterized by $\Omega = 10^8 \text{ cm}^{-2} \text{ sec}^{-1}$ and the reduced sweep-rate parameter $\frac{s^3}{\Omega k_1^2} = 10^{-5} \text{ V}^3 \text{ cm}^2.$

[The maxima in C for the overall curves in (a) and (b) have been calculated to arise at the same (peak) potentials by appropriate choice of numerical values for the two cases; hence the particular values for N_0 and $\frac{1}{N_0} \left(\frac{s}{k_1} \right)^2$ in (a)].



The main features are as follows:

- (i) For the potentiostatic case, formation of a current peak characterized by $i_p t_p = \text{constant}$ is observed; a common curve of the reduced values i/i_p and t/t_p can be derived.
- (ii) For the potentiodynamic case, a current peak is always observed but has a characteristic shape only for totally irreversible conditions in the growth reaction [2].
- (iii) Peak parameters and the half-widths have characteristic values (Table 10-2).
- (iv) The overall kinetic constant for the process and the value of β (or the Tafel slope) for the growth reaction can be evaluated from the parameters of the irreversible current peak in the potentiodynamic case and from the peak parameters i_p and t_p for the potentiostatic case.

APPENDIX I

LISTING OF THE COMPLETE COMPUTER PROGRAMME USED FOR
SIMULATION OF CURRENT-POTENTIAL PROFILES FOR DIFFERENT
REACTION MECHANISMS

The programme appearing in this Appendix (I) is a representative one. For simplicity, the programme for a simple 1-e electrochemical reaction is shown. This means that the statements appearing in Section 3 of the S/360 CSMP programme below are those for differential equations describing the above mentioned reaction mechanism treated in Chapter IV. For the various processes considered, different set of statement cards in Section 3 is needed to describe the appropriate differential equations necessary to simulate given reaction mechanisms. Various conditions for a given reaction mechanism are treated by changing the appropriate variable parameters (e.g., sweep rate, rate constants, etc.) in the data statements appearing in Section 2. Also, the execution and output control statements, which are embodied in Section 4, may change from one reaction mechanism to another. Hence, the statements appearing in these three sections refer only to a given reaction mechanism and/or of particular run in question.

The other sections of the S/360 CSMP programme (i.e., Sections 1, 5, 6 and 7) and all the supplied subroutines remain unchanged for all the reaction mechanisms studied in this thesis.

A detailed description of the overall representative computer programme, listed on the following pages, was given in Chapter III.

CONTINUOUS SYSTEM MODELING PROGRAM
 PROBLEM INPUT STATEMENTS

 * THIS PROGRAMME SOLVES UP TO 5 ELECTRUCHEMICAL AND/OR CHEMICAL REACTIONS *
 * BOTH IN PARALLEL AND/OR IN SERIES USING APPROPRIATE SET *
 * OF DIFFERENTIAL EQUATIONS *

 * SECTION 1 *

// DIMENSION GFF(5),GFB(5),PREVI(5),FLIP(5),TEMPI(5),THTEMP(5)
 // DIMENSION A(5),BF(5),QB(5),CF(5),CB(5),XVAR(500),YVAR(500),NAME(5)
 // DIMENSION GTF(5),GTB(5)
 // DATA NAME//ITUT//SR//VS//VOLT//AGE//
 // EQUIVALENCE (TEMPI(1),1),(THTEMP(1),TH1)
 // FIXED FLAG,KEEP,K,ICOUNT,IDIR,NDIM,FLIP,KK,LL,J,NPRL,INHOLD
 // CONST FC=96490.,BETA=0.5,R=8.314J,TP=298.15,CPCM=0.00022
 // STORAGE FRC(5),BRC(5),ER(5),SIGN(5),EN(5),G(5)

 * SECTION 2 *

 * ALL THE RELEVANT DATA ARE ENTERED HERE *

TABLE FRC(1)=0.1,BRC(1)=0.1,ER(1)=0.0,SIGN(1)=1.0,EN(1)=1.0,G(1)=0.0
 INCON IDIR=1,NDIM=1,NPRL=1,TH1=0.0
 PARAM SR=1.0,VIN=-0.2,VAEND=0.5,VLEND=-0.4,...
 ICGUNT=2,CMULT=-1.0,VCUT=0.4,...
 I HOLD=0,VHOLD=0.0,THOLD=0.0

 * SECTION 3 *

 * *****

```

*
* THIS MACRO FUNCTION 'SOLVE' DEFINES THE DIFFERENTIAL EQUATIONS TO BE
*
* USED FOR CALCULATIONS OF COVERAGES, TOTAL COVERAGE, CURRENTS,
*
* TOTAL CURRENT AND TOTAL CAPACITANCE AS A FUNCTION OF POTENTIAL
*
*****

```

```

MACRO THET1, THET2, THET3, THET4, THET5, DER1, DER2, DER3, DER4, DER5=...
  DF1=FRC(1)*CF(1)*(1.0-THET1)
  DB1=BRC(1)*CB(1)*THET1
  D1=DF1-DB1
  DTH1=SIGN(1)*D1
  THET1=INTGR1(TH1, DTH1)
  DER1=DTH1*CPCM
ENDMAC

```

```

*****
*****
***** SECTION 4 *****
*****

```

```

METHOD RKS
TIMER FINTIM=1.0E 04, DELT=1.0E-03, DELMIN=1.0E-08
FINISH IEND=1.0
RANGE VOLT, IDS, I1, I2, I3, I4, I5
RELERR VOLT=1.0E-07, THET1=1.0E-08
AUSERR VOLT=1.0E-07, THET1=1.0E-08
PRINT TH1, VOLT, I, IDS
TITLE REVERSIBLE 1 ELECTRON ELECTROCHEMICAL REACTION

```

```

*****
*****
***** SECTION 5 *****
*****

```

INITIAL

NOSCR

```

AA=FC/(R*TP)
IF(IDIR.EQ.-1) AA=-AA
BETA1=1.0-BETA
CONSTF=BETA*AA
CONSTB=BETA1*AA
SR=FLCAT(IDIR)*ABS(SR)
CALL INITH
DC 10 K=1, NDIM
PREV1(N)=0.0
FLIP(K)=0
GF(K)=BETA*G(K)
GFU(K)=BETA1*G(K)

```

```

EN(K)=FLOAT(IDIR)*EN(K)
10 CONTINUE
KK=0
LL=0
ITOTPR=0.0
FLAG=0
J=0
SW1=1.0
IEND=C.0
PRDEL=0.001/ABS(SR)
DLIT=0.1*PRDEL
OUTDEL=0.001/ABS(SR)

```

```
*****  
SECTION 6  
*****
```

DYNAMIC

WJSDRT

```

TH1=THET1
TH2=THET2
TH3=THET3
TH4=THET4
TH5=THET5
TH=TH1+TH2+TH3+TH4+TH5
VOLT=MODINT(VIN,SW1,-1.0,SR)
DO 20 K=1,NDIM
  GTF(K)=THTEMP(K)*GFF(K)
  GTB(K)=THTEMP(K)*GTB(K)
  IF(EN(K).EQ.0.0) GO TO 15
  A(K)=VOLT-ET(K)
  BF(K)=(A(K)*CONSTF)-GTF(K)
  CF(K)=EXP(BF(K))
  BE(K)=(-CONSTB*(K))+GTB(K)
  CB(K)=EXP(BE(K))
  GO TO 20
15 CF(K)=EXP(-GTF(K))
  CU(K)=EXP(GTB(K))
20 CONTINUE

```

TICS

```

THET1, THET2, THET3, THET4, THET5, DER1, DER2, DER3, DER4, DER5=...
      SOLVE(FKC, BKC, SIGN, CF, CB, CPCM, FC)
      I1=DER1*SIGN(1)*EN(1)
      I2=DER2*SIGN(2)*EN(2)
      I3=DER3*SIGN(3)*EN(3)
      I4=DER4*SIGN(4)*EN(4)
      I5=DER5*SIGN(5)*EN(5)
      I=I1+I2+I3+I4+I5
      IDS=I/ABS(5K)

```

NOTES

```

IF(KEEP.EQ.0) GO TO 66
IF(IJ.LT.2).OR.(KK.GT.9) GO TO 62
IF(ABS(IDS).LT.0.00015) GO TO 62
CALL PEAKS(NDIM,FLAG,ITUTPR,I,VOLT,TH,THTEMP,SR,FLIP,PKEVI,...,
TEMP1,KK,LL)
62 CONTINUE
IF(IJ.EQ.0) GO TO 64
IF(ICCUNT.LE.2) GO TO 63
IF(ABS(VOLT-VCUT).GE.0.0005) GO TO 63
IF(ABS(VOLT-XVAR(J)).LT.0.0005) GO TO 65
CALL PRINT
GO TO 64
63 IF(ABS(VOLT-XVAR(J)).LT.0.0005) GO TO 65
64 J=J+1
XVAR(J)=VOLT
YVAR(J)=IDS
65 CONTINUE
CALL FCNGEN(IHOLD,IDIR,ICOUNT,SM1,VOLT,VHOLD,VCUT,TIME,SR,...,
THOLD,CAULT,VAEND,VCEND,PRODEL,JUTDEL,DEL,IEND)
66 CONTINUE

```

[illegible]

```

IF(ICOUNT.GT.2) SR=SR/CMULT
CALL CPUTUT
CALL PLTDET(YVAR,J.IDIR,ICOUNT,VIN,VAEND,VCEND,XMIN,XMAX,YMIN,...
            YMAX)
CALL GRAPH(XVAR,YVAR,J.NAME,XMIN,XMAX,YMIN,YMAX)
CALL RENEW

```

* * * * *

END
STOP

```

OUTPUT VARIABLE SEQUENCE
AA AA BETA1 CONSTB SR Z20007 KK LL ITOTPR
J S*1 IEND PKDEL DELT OUTDEL TH1 TH2 TH3
THS TH Z20009 VOLT VGLT Z20011 Z20012 Z20014 Z20013
Z20015 THET1 15 14 13 DER1 I
IDS Z20018 J SR Z20019

PARAMETERS NOT INPUT OR OUTPUTS NOT AVAILABLE TO SORT SECTION**SET TO ZERO***
THET2 THET3 THET4 THETS DER2 DER3 DER4 DER5

OUTPUTS INPUTS PARAMS INTEG + MEM BLKS FUNTRAN DATA CDS
S9(5C0) 85(140C) 32(4CC) 2+ 0= 2(J00) 87(6C0) 15

```

END PAGE


```

0039
0040
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0042
0043
0044

FORTRAN IV G LEVEL 21
C....
DO 11 K=1,NPRL
  TH(K)=THISTR(K)
  IF(ICCUNT.GT.2) ICCOUNT=2
  IF(IAUS(IHOLD).EQ.2) IHOLD=IHOLD/2
  RETURN
END

INIT 370
INIT 380
INIT 390
INIT 400
INIT 410
INIT 420
INIT 430

DATE = 76320
20/19/52
PAGE 0002
```



```
0041
0042
0043
0044
0045

FORTRAN IV G LEVEL 21          FCNGEN          DATE = 76320          PAGE 0002
                                CATHODIC POTENTIALS AND IF THIS IS NOT SO IT
                                STOPS THE PROGRAMME.
                                20/19/52
                                FCNG 590
                                FCNG 600
                                FCNG 610
                                FCNG 620
                                FCNG 630
                                FCNG 640
                                FCNG 650
                                FCNG 660

C
C.....
15 IF(VOLT-VCEND) 17,18,19
16 IF(VOLT-VAEND) 18,18,17
17 IEND=1.0
18 RETURN
END
```

```

FORTRAN IV G LEVEL 21
0001
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SUBROUTINE PEAKS(NDIM,FLAG,ITOTPR,I,VCLT,TH,THTEMP,SR,FLIP,IPREV,
$ITEMP,KK,LL)
DIMENSION PTHPRV(5),PIPRV(5),THTEMP(5),ITEMP(5),IPREV(5),VPREV(5),
$THPREV(5),FLIP(5)
COMMON/AREA1/VTPEAK(10),ITPEAK(10),THPK(10),THCOPK(10,5),
$ICCPK(10,5),VPEAK(10),IPEAK(10),THPEAK(10),JJ(10),
REAL ITEM,ITPEAK,IPEAK,IPREV,ITOTPR,I,ICUPK
INTEGER FLAG,FLIP
C.....
C
C
C.....
MAXIMA AND MINIMA OF THE CURRENT-POTENTIAL CURVES ARE
DETERMINED BY THIS SUBROUTINE.
ICOND=1
IF(SR.LT.0.0) ICCND=-1
IF(FLAG.EQ.1) GO TO 60
IF(((ITOTPR.GT.1).AND.(ICOND.EQ.1)).OR.((ITOTPR.LT.1).AND.(ICOND.
$EQ.-1))) GO TO 52
ITOTPR=1
VOTPR=VOLT
THTPR=TH
IF(NDIM.EQ.1) GO TO 62
DO 51 K=1,NDIM
PIPRV(K)=ITEMP(K)
PTHPRV(K)=THTEMP(K)
51 GO TO 56
52 KK=KK+1
VTPEAK(KK)=VOTPR
ITPEAK(KK)=ITOTPR
THPK(KK)=THTPR
IF(NDIM.EQ.1) GO TO 54
DO 53 K=1,NDIM
ICOPK(KK,K)=PIPRV(K)
THCOPK(KK,K)=PTHPRV(K)
53 FLAG=1
54 IF(NDIM.EQ.1) GO TO 62
55 DO 55 K=1,NDIM
IF(LL.GT.9) GO TO 59
IF(ABS(ITEMP(K)/SR).LT.0.00005) GO TO 59
IF(FLIP(K).EQ.1) GO TO 58
IF(((IPREV(K).GT.ITEMP(K)).AND.(ICOND.EQ.1)).OR.((IPREV(K).LT.
$ITEMP(K)).AND.(ICOND.EQ.-1))) GO TO 57
IPREV(K)=ITEMP(K)
VPREV(K)=VOLT
THPREV(K)=THTEMP(K)
GO TO 59
57 LL=LL+1
VPREV(LL)=VPREV(K)
IPEAK(LL)=IPREV(K)
THPEAK(LL)=THPREV(K)
JJ(LL)=K
FLIP(K)=1
GO TO 59
58 IF(((IPREV(K).GT.ITEMP(K)).AND.(ICOND.EQ.1)).OR.((IPREV(K).LT.
$ITEMP(K)).AND.(ICOND.EQ.-1))) GO TO 59
IPREV(K)=ITEMP(K)
FLIP(K)=0
59 CONTINUE
GO TO 62
PEAK 10
PEAK 20
PEAK 30
PEAK 40
PEAK 50
PEAK 60
PEAK 70
PEAK 80
PEAK 90
PEAK 100
PEAK 110
PEAK 120
PEAK 130
PEAK 140
PEAK 150
PEAK 160
PEAK 170
PEAK 180
PEAK 190
PEAK 200
PEAK 210
PEAK 220
PEAK 230
PEAK 240
PEAK 250
PEAK 260
PEAK 270
PEAK 280
PEAK 290
PEAK 300
PEAK 310
PEAK 320
PEAK 330
PEAK 340
PEAK 350
PEAK 360
PEAK 370
PEAK 380
PEAK 390
PEAK 400
PEAK 410
PEAK 420
PEAK 430
PEAK 440
PEAK 450
PEAK 460
PEAK 470
PEAK 480
PEAK 490
PEAK 500
PEAK 510
PEAK 520
PEAK 530
PEAK 540
PEAK 550
PEAK 560
PEAK 570
PEAK 580

```



```

0049      FORTTRAN IV G LEVEL 21
0050      60 IF(((ITOTPR-GT.I).AND.(ICOND.EQ.I)).OR.((ITOTPR.LT.I).AND.(ICOND.
0051          $EG.-I))) GO TO 61
0052      61 ITOTPR=I
0053          FLAG=0
0054      62 RETURN
0055      END
0056
0057      PEAKS
0058      20/19/52
0059      DATE = 76320
0060      PAGE 0002
0061      PEAK 590
0062      PEAK 600
0063      PEAK 610
0064      PEAK 620
0065      PEAK 630
0066      PEAK 640
0067      PEAK 650

```

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FORTTRAN IV G LEVEL 21          PRINT          DATE = 76320          20/19/52          PAGE 0001

0001      SUBROUTINE PRINT
0002      COMMON DA(8000),DB(976),NGRAPH,KGRAPH,DC(728),IEND

C.....
C      ADDITIONAL POINTS,BESIDES THOSE REQUESTED IN A PARTICULAR
C      SIMULATION RUN,MAY BE OBTAINED BY CALLING SUBROUTINE PRINT.
C.....

0003      NSAVE=NGRAPH
0004      KSAVE=KGRAPH
0005      IEND=-1
0006      CALL SIMCUT
0007      IEND=0
0008      NGRAPH=NSAVE
0009      KGRAPH=KSAVE
0010      RETURN
0011      END

PRIN 10
PRIN 20
PRIN 30
PRIN 40
PRIN 50
PRIN 60
PRIN 70
PRIN 80
PRIN 90
PRIN 100
PRIN 110
PRIN 120
PRIN 130
PRIN 140
PRIN 150

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0001 SUBROUTINE OUTPUT
0002 COMMON ZZ9901(5), IZ9901, ZZ9902, IZ9902, ZZ9903, IZ9903, ZZ9904(54)
0003 COMMON TIME
1, DELT, DELMIN, FINTIM, PROEL, GUIDEL, VOLT, THET1, ZZ0011, ZZ0016
1, VIN, TH1, ZZ0008, FC, BETA, R, TP, CPCM, IDIR
1, NDIM, NPRL, SR, VAEND, VGEN, ICOUNT, CMULT, VCUT, IHULU
1, VHOLD, THOLD, THET3, THET4, THET5, DER2, DER3, DER4
1, DERS, AA, BETA1, CONSTF, CONSTB, ZZ0007, KK, LL, ATOTPR
1, FLAG, J, SW1, IEND, TH1, TH2, TH3, TH4, TH5
1, TH, ZZ0009, ZZ0012, ZZ0013, ZZ0014, ZZ0015, DLR1, I1, I2
1, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12
1, IZ0003, IZ0004, IZ0005, IZ0006
COMMON FRC ( 5)
COMMON ERC ( 5)
COMMON ER ( 5)
COMMON SIGN ( 5)
COMMON EN ( 5)
COMMON G ( 5)
COMMON ZZ9992(7853), NALARM, IZ9993, ZZ9994(417), KEEP, ZZ9995(489)
COMMON ZZ9996(824), IZ9997, IZ9998, ZZ9999( 146)
REAL ITOTPR
1, IEND, I1, I2, I3, I4, I5, I6, I7, I8, I9, I10, I11, I12
1, INTEGER, FLAG
1, FLIP
COMMON/AREA1/TYPEAK(10), TPEAK(10), THPK(10), THCPK(10.5),
SCOIPK(10.5), SVPEAK(10), SIFEAK(10), STHPK(10), JJ(10)
C..... THIS SUBROUTINE PRINTS THE VALUES OF VARIOUS PARAMETERS USED
C AND THE RESULTS OBTAINED BY SUBROUTINE PEAKS.
C.....
0014 WRITE(6,104)
0015 104 FORMAT(1//,10X,'RATE CONSTANTS, CORRESPONDING REVERSIBLE POTENTIAL',
$EN,16X,'G,')
DC 25 K=1,NDIM
IF (EN(K).EQ.0.0) GO TO 24
WRITE(6,109) K, FRC(K), ERC(K), ER(K), EN(K), G(K)
109 FORMAT(10X,13.2X,1PE12.4,7X,1PE12.4,8X,0PF10.4,8X,0PF8.2,12X,
$OPF7.3)
GO TO 25
24 WRITE(6,110) K, FRC(K), ERC(K), G(K)
110 FORMAT(10X,13.2X,1PE12.4,7X,1PE12.4,14X,'CHEMICAL REACTION',15X,
$OPF7.3)
25 CONTINUE
105 FCRMAT(10X,13.2X,1PE12.4,7X,1PE12.4,10X,'V-ANODIC ENDS',F8.4,10X,'V-CATHODIC
ENDS',F8.4)
WRITE(6,106) IDIR, SR
106 FCRMAT(10X,10X,1DIR=,13,10X,'SWEEP RATE',F9.4,' VOLTS/SEC')
IF (ICOUNT.LE.2) GO TO 39
WRITE(6,108) CMULT, VCUT
108 FCRMAT(10X,'MULT.CONSTANT FOR S=',F12.5,10X,'VCUT=',F10.4)
39 CONTINUE
IF (IARS(IHOLD),LT.2) GO TO 40
WRITE(6,111) IHOLD, VHOLD, THOLD
111 FCRMAT(10X,'INCLUDE',13,10X,'V-HOLDING=',F8.4,10X,'HOLDING TIME',
$F10.4)
40 CONTINUE
0035

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OUTP 30
 OUTP 40
 OUTP 50
 OUTP 60
 OUTP 70
 OUTP 80
 OUTP 90
 OUTP 100
 OUTP 110
 OUTP 120
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 OUTP 330
 OUTP 340
 OUTP 350
 OUTP 360

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0036      IF(KK.EQ.0) GO TO 81
0037      DC 80 K=1,KK
0038      WRITE(6,112) K,TVPEAK(K),TIPEAK(K),THPK(K)
0039      112  FORMAT(/10X,'PEAK NO.=',I3.5X,'TOTAL V-PEAK=',0PF8.4.5X,'TOTAL I-PEAK=',0PF7.4)
0040      IF(NDIM.EQ.1) GO TO 80
0041      WRITE(6,114) (K,CUIPK(K,KC),KC,THCOPK(K,KC),KC=1,NDIM)
0042      114  FORMAT(5X,'I(',I2.1,')=',1PE12.4.12X,'TH(',I2.1,')=',0PF7.4)
0043      80  CONTINUE
0044      GO TO 82
0045      81  WRITE(6,116)
0046      116  FORMAT(/10X,'NO PEAK OBSERVED')
0047      82  IF(NDIM.EQ.1) GO TO 83
0048      IF(LL.EQ.0) GO TO 83
0049      115  WRITE(6,115) (K,JJ(K),SVPEAK(K),SIPEAK(K),STHPK(K),K=1,LL)
0050      115  FORMAT(/10X,'REACTION',5X,'V-PEAK',5X,'I-PEAK',5X,'TH-PEAK',//)
0051      83  CONTINUE
0052      RETURN
0053      END

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OUTPUT

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FORTTRAN IV G LEVEL

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FORTRAN IV G LEVEL 21          PLTDET          DATE = 76320          20/19/52          PAGE 0001

0001      SUBROUTINE PLTDET(YVAR,J,DIR,ICOUNT,VIN,VAEND,VCEND,XXMIN,XXMAX, PLTD 10
0002      SYMIN,YYMAX)          PLTD 20
          DIMENSION YVAR(1)          PLTD 30
          C.....          PLTD 40
          C          MAXIMA AND MINIMA FOR THE GRAPH TO BE PLOTTED ARE DEFINED          PLTD 50
          C          BY THIS SUBROUTINE.          PLTD 60
          C.....          PLTD 70
          YMIN=YVAR(1)          PLTD 80
          YMAX=YVAR(1)          PLTD 90
          DO 44 K=2,J          PLTD 100
            IF(YMAX-YVAR(K)) 41,41,42          PLTD 110
            YMAX=YVAR(K)          PLTD 120
            IF(YMIN-YVAR(K)) 44,43,43          PLTD 130
            YMIN=YVAR(K)          PLTD 140
            44 CONTINUE          PLTD 150
            IF(DIR.EQ.-1) GO TO 55          PLTD 160
            XXMIN=VIN          PLTD 170
            YYMIN=0.0          PLTD 180
            YYMAX=0.0015          PLTD 190
            51 IF(YYMAX.GT.YMAX) GO TO 52          PLTD 200
            YYMAX=2.0*YYMAX          PLTD 210
            GO TO 51          PLTD 220
            52 IF((YYMAX/3.0).LT.YMAX) GO TO 53          PLTD 230
            YYMAX=YYMAX/2.0          PLTD 240
            GO TO 52          PLTD 250
            53 IF(ICOUNT.NE.J) GO TO 54          PLTD 260
            IF(VCEND.LT.VIN) XXMIN=VCEND          PLTD 270
            YYMIN=YYMAX          PLTD 280
            54 XXMAX=XXMIN+1.0          PLTD 290
            GO TO 60          PLTD 300
            55 XXMAX=VIN          PLTD 310
            YYMAX=C.0          PLTD 320
            YYMIN=-C.0015          PLTD 330
            56 IF(YYMIN.LT.YMIN) GO TO 57          PLTD 340
            YYMIN=2.0*YYMIN          PLTD 350
            GO TO 56          PLTD 360
            57 IF((YYMIN/3.0).GT.YMIN) GO TO 58          PLTD 370
            YYMIN=YYMIN/2.0          PLTD 380
            GO TO 57          PLTD 390
            58 IF(ICOUNT.NE.J) GO TO 59          PLTD 400
            IF(VAEND.GT.VIN) XXMAX=VAEND          PLTD 410
            YYMAX=-YYMIN          PLTD 420
            59 XXMIN=XXMAX-1.0          PLTD 430
            60 RETURN          PLTD 440
          END          PLTD 450

```

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FORTRAN IV G LEVEL 21          GRAPH          DATE = 76320          PAGE 0001

0001      SUBROUTINE GRAPH(X,Y,N,TITLE,XMIN,XMAX,YMIN,YMAX)
C..... THIS SUBROUTINE PLOTS A GRAPH OF A GIVEN FUNCTION
C.....
0002      DIMENSION X(N),Y(N),TITLE(5),XSCAL(11),YSCAL(10)
0003      LOGICAL*1 ARRAY(101,55),BLANK/0,STAR/'*'/
C..... INITIALIZE ARRAY,AND SCALE FACTORS XSF,YSF
C.....
0004      DO 10 I=1,101
0005      DO 10 J=1,55
0006      ARRAY(I,J)=BLANK
0007      YSF=(YMAX-YMIN)/54.0
0008      XSF=(XMAX-XMIN)/100.0
C.....
C..... FILL PRINT SQUARES WITH ASTERISKS TO FORM GRAPH
C.....
0009      DO 100 K=1,N
0010      I=(X(K)-XMIN)/XSF+1.5
0011      J=(Y(K)-YMIN)/YSF+1.5
0012      IF(I.GT.101.OR.I.LT.1) GO TO 100
0013      IF(J.GT.55.OR.J.LT.1) GO TO 100
0014      ARRAY(I,J)=STAR
0015      CC CONTINUE
C.....
C..... SKIP TO NEW PAGE , PRINT TITLE AND CALCULATE SCALE INDICATORS
C.....
0016      WRITE(6,1) TITLE
0017      1 FORMAT(1,/,/,55X,5A4)
0018      DO 110 I=1,11
0019      XSCAL(I)=XMIN+XSF*(10*I-10)
0020      DO 120 J=1,10
0021      YSCAL(J)=YMIN+YSF*(6*J-6)
C.....
C..... PRINT GRAPH LINE BY LINE
C.....
0022      DO 200 J=1,55
0023      IF(MOD(J,6).EQ.1) GO TO 150
0024      WRITE(6,2) (ARRAY(I,56-J),I=1,101)
0025      2 FORMAT(13X,/,/,101A1)
0026      GO TO 200
0027      150 WRITE(6,3) YSCAL(10-J/6),(ARRAY(I,56-J),I=1,101)
0028      3 FORMAT(1X,1PE12.4,/,/,101A1)
0029      200 CONTINUE
0030      WRITE(6,4) XSCAL
0031      4 FORMAT(14X,10(1,-----),1,/,8X,11F10.4)
0032      RETURN
0033      END
GRAP 10
GRAP 20
GRAP 30
GRAP 40
GRAP 50
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GRAP 370
GRAP 380
GRAP 390
GRAP 400
GRAP 410
GRAP 420
GRAP 430
GRAP 440
GRAP 450
GRAP 460
GRAP 470
GRAP 480

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0045 PREVI(K)=0.0
0046 FLIP(K)=0
0047 GFF(K)=BETA*G(K)
0048 GFB(K)=BETA1*G(K)
0049 EN(K)=FLCAT(IDIR)*EN(K)
0050 CCNTINUE
0051 KK=0
0052 LL=0
0053 ITOTFR=0.0
0054 FLAG=0
0055 J=0
0056 SW1=1.0
0057 IEND=C.0
0058 PROEL=0.001/ABS(SR)
0059 DELT=0.1*PROEL
0060 OUTDEL=0.001/ABS(SR)
0061 GO TO 3955
C DYNAMIC SEGMENT OF MODEL
3957 CCNTINUE
0062 TH1=TFET1
0063 TH2=TFET2
0064 TH3=TFET3
0065 TH4=TFET4
0066 TH5=TFET5
0067 TH=TH1+TH2+TH3+TH4+TH5
0068 Z20009=FCNSW(Z20008,VCLT,VCLT,VIN)
0069 VOLT=FCNSW(SW1,Z20009,Z20009,VOLT)
0070 VCLT=INTGRL(VIN)
C
0071 Z20011=FCNSW(SW1,0.0,0.0,SR)
0072 DO 20 K=1,NDIM
0073 GTF(K)=THTEMP(K)*GFF(K)
0074 GTB(K)=THTEMP(K)*GFB(K)
0075 IF(EN(N).EQ.0.0)GO TO 15
0076 A(K)=VCLT-ER(K)
0077 BF(K)=(A(K)*CONSTF)-GTF(K)
0078 CF(K)=EXP(BF(K))
0079 EB(K)=(-CONSTB*A(K))+GTB(K)
0080 CB(K)=EXP(CB(K))
0081 GO TO 20
0082 CF(K)=EXP(-GTF(K))
0083 CB(K)=EXP(GTB(K))
0084 CCNTINUE
0085 Z20014=URC(1)*CB(1)*THET1
0086 Z20013=PRC(1)*CF(1)*(1.0-THET1)
0087 Z20015=Z20013-Z20014
0088 Z20016=SIGN(1)*Z20015
0089 THET1=INTGRL(TH1)
0090 I5=DER5*SIGN(5)*EN(5)
0091 I4=DER4*SIGN(4)*EN(4)
0092 I3=DER3*SIGN(3)*EN(3)
0093 I2=DER2*SIGN(2)*EN(2)
0094 DER1=Z20016*CPCM
0095 I1=DER1*SIGN(1)*EN(1)
0096 I=I1+I2+I3+I4+I5
0097 IDS=1/ABS(SR)
0098 IF(KEEP.EQ.0)GO TO 66
0099 IF((J.LT.2).OR.(KK.GT.9))GO TO 62
0100 IF(AUS(IDS).LT.0.00015)GO TO 62

```



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FORTRAN IV G LEVEL 21
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0123
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        CALL PEAKS(NDIM,FLAG,ITGTPR,I,VOLT,TH,IHTEMP,SR,FLIP,PREVI,TEMP1,
        $ KK,LL)
        CONTINUE
        IF(J.EC.0)GO TO 64
        IF(ICCUNT.LE.2)GO TO 63
        IF(ABS(VCLT-VCUT).GE.0.005)GO TO 63
        IF(ABS(VOLT-XVAR(J)).LT.0.0005)GO TO 65
        CALL PRINT
        GO TO 64
        63 IF(ABS(VCLT-XVAR(J)).LT.0.005)GO TO 65
        64 J=J+1
        XVAR(J)=VCLT
        YVAR(J)=IDS
        CONTINUE
        65 CALL FCNGEN(IHOLD,IDIR,ICCUNT,SW1,VOLT,VHOLD,VCUT,TIME,SR,THOLD,
        $ CMULT,VAEND,VCEND,PRDEL,OUTDEL,DELT,IEND)
        CONTINUE
        GO TO 39359
C TERMINAL SEGMENT OF MODEL
39358 CONTINUE
        IF(ICCUNT.GT.2)SR=SR/CMULT
        CALL CUTPUT
        CALL PLTDET(YVAR,J,IDIR,ICCUNT,VIN,VAEND,VCEND,XMIN,XMAX,YMIN,YMAX
        $)
        CALL GRAPH(XVAR,YVAR,J,NAME,XMIN,XMAX,YMIN,YMAX)
        CALL RENEW
39999 CONTINUE
        RETURN
        END
    
```

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APPENDIX II

DERIVATION OF THE ANALYTICAL EQUATION (4-13) USED FOR DETERMINATION OF COVERAGE $\theta_{B,p}$ AT THE MAXIMUM OF C-V PROFILES FOR AN IRREVERSIBLE 1-e ELECTROCHEMICAL REACTION WHEN $g \neq 0$

Noting from eqn. (4-8) (p. 95) that

$$\frac{i}{Q} = \frac{d\theta_B}{dt}, \quad (A2-1)$$

integration may be performed giving

$$\int \frac{\exp[(1-\beta)g\theta_B]}{1-\theta_B} d\theta_B = \frac{k_1 b}{s} \exp\left(\frac{\Delta V}{b}\right) + IC \quad (A2-2)$$

where $b = \frac{RT}{\beta F}$ (see Chapter IV, p. 94) and IC is an integration constant. The l.h.s. of eqn. (A2-2) may be evaluated with the aid of the following formula

$$\int \frac{\exp(ax)}{x} dx = \ln x + \frac{ax}{1.1!} + \frac{(ax)^2}{2.2!} + \frac{(ax)^3}{3.3!} + \dots = \ln x + \sum_{n=1}^{\infty} \frac{(ax)^n}{n.n!} \quad (A2-3)$$

Defining $1-\theta_B$ as x [cf. eqn. (A2-2)] so that $d\theta_B = -dx$ and then integrating the l.h.s. of eqn. (A2-2) gives

$$\int \frac{\exp[(1-\beta)g\theta_B]}{1-\theta_B} d\theta_B = -\exp[(1-\beta)g]\left\{\ln(1-\theta_B) + \sum_{n=1}^{\infty} \frac{[-(1-\beta)g(1-\theta_B)]^n}{n.n!}\right\} \quad (A2-4)$$

Substituting now eqn. (A2-4) into eqn. (A2-2), the following expression is obtained:

$$-\exp[(1-\beta)g]\{\ln(1-\theta_B) + \sum_{n=1}^{\infty} \frac{[-(1-\beta)g(1-\theta_B)]^n}{n \cdot n!}\} = \frac{k_1 b}{s} \exp(\frac{\Delta V}{b}) + IC \quad (A2-5)$$

IC is evaluated from the boundary condition $\theta_B = 0$ at $t=0$ in the sweep, i.e., when the potential V is $V = V_{in}$, the initial potential in the sweep. Then

$$\begin{aligned} \ln(1-\theta_B) &= \frac{k_1 b}{s} \exp[-(1-\beta)g] [\exp(\frac{\Delta V_{in}}{b}) - \exp(\frac{\Delta V}{b})] \\ &- \sum_{n=1}^{\infty} \frac{[-(1-\beta)g]^n}{n \cdot n!} [(1-\theta_B)^n - 1] \end{aligned} \quad (A2-6)$$

where ΔV_{in} is defined as

$$\Delta V_{in} = V_{in} - E^\circ \quad (A2-7)$$

Substituting $\ln(1-\theta_B)$ from eqn. (A2-6) into eqn. (4-8) in logarithmic form, enables $\ln i$ to be obtained as

$$\begin{aligned} \ln i &= \ln Qk_1 + \frac{k_1 b}{s} \exp[-(1-\beta)g] [\exp(\frac{\Delta V_{in}}{b}) - \exp(\frac{\Delta V}{b})] - \\ &\sum_{n=1}^{\infty} \frac{[-(1-\beta)g]^n}{n \cdot n!} [(1-\theta_B)^n - 1] + \frac{\Delta V}{b} - (1-\beta)g\theta_B \end{aligned} \quad (A2-8)$$

In order to obtain the value of i_p , V_p from eqn. (4-11) is substituted into eqn. (A2-8), giving

$$\begin{aligned} \ln i_p &= \ln Qk_1 + \exp[-(1-\beta)g] [\frac{k_1 b}{s} \exp(\frac{\Delta V_{in}}{b}) - \frac{\exp[(1-\beta)g\theta_{B,p}]}{1+(1-\beta)g(1-\theta_{B,p})}] \\ &+ \ln \frac{s}{k_1 b} - \ln[1+(1-\beta)g(1-\theta_{B,p})] - \sum_{n=1}^{\infty} \frac{[-(1-\beta)g]^n}{n \cdot n!} [(1-\theta_{B,p})^n - 1] \end{aligned} \quad (A2-9)$$

After combining appropriate ln terms and rearranging, and noting that for an irreversible process where $\frac{s}{k_1} \gg 1$,

$$\frac{k_1 b}{s} \exp\left(\frac{\Delta V_{in}}{b}\right) << \frac{\exp[(1-\beta)g\theta_{B,p}]}{1+(1-\beta)g(1-\theta_{B,p})} \quad (A2-10)$$

it is found that i_p is given by

$$i_p = \frac{Q_s}{b[1+(1-\beta)g(1-\theta_{B,p})]} \exp\left\{-\frac{\exp[-(1-\beta)g(1-\theta_{B,p})]}{1+(1-\beta)g(1-\theta_{B,p})}\right\} - \sum_{n=1}^{\infty} \frac{[-(1-\beta)g]^n}{n \cdot n!} [(1-\theta_{B,p})^n - 1] \quad (A2-11)$$

Comparison of eqn. (4-10) with (A2-11) shows that the coverage $\theta_{B,p}$, corresponding to the peak i_p , is given by

$$\theta_{B,p} = 1 - \exp\left\{-\frac{\exp[-(1-\beta)g(1-\theta_{B,p})]}{1 + (1-\beta)g(1-\theta_{B,p})}\right\} - \sum_{n=1}^{\infty} \frac{[-(1-\beta)g]^n}{n \cdot n!} [(1-\theta_{B,p})^n - 1] \quad (A2-12)$$

The above equation (A2-12), which is identical with eqn. (4-13) (cf. p. 96), was solved numerically by an iterative method until a convergent solution for $\theta_{B,p}$ was obtained for a given g parameter. The results of this derivation were used in Chapter IV to check the numerical evaluation of $\theta_{B,p}$ as a function of g shown in Fig. 4-7.

APPENDIX III

PROOF OF SIMILARITY OF C-V PROFILES FOR AN
IRREVERSIBLE 1-e ELECTROCHEMICAL SURFACE PROCESS WITH $g = 0$

It is clear from the numerically derived C-V profiles for the irreversible reaction (I) (cf. Chapter IV, Fig. 4-1), that they are of identical form, independent of the sweep-rate, s . It is of interest to prove this.

A new potential scale V_{sc} referred to the peak potential of any curve will be defined as

$$V_{sc} = V - V_p \quad (A3-1)$$

or in the anodic-going linear potential sweep as

$$V_{sc} = V_{in} + st - V_p \quad (A3-2)$$

Substituting eqn. (A3-1) and eqn. (4-2) for an anodic-going sweep (p. 93) into eqn. (4-8) (p. 95) for $g = 0$ and writing eqn. (4-8) as

$$\frac{i}{Q} = \frac{d\theta_B}{dt}, \quad (A3-3)$$

enables the integration

$$\int \frac{d\theta_B}{1-\theta_B} = \int k_1 \exp\left(\frac{V_{sc} + V_p - E^\circ}{b}\right) dt \quad (A3-4)$$

to be performed. Thus,

$$- \ln (1-\theta_B) = \frac{k_1 b}{s} \exp\left(\frac{V_{sc} + V_p - E^\circ}{b}\right) + IC' \quad (A3-5)$$

knowing that V_{sc} in eqn. (A3-4) contains the term st. The potential V_p is given by eqn. (4-11), which for $g = 0$ reduces⁹⁰ to

$$V_p = b \ln \frac{s}{k_1 b} + E^\circ \quad (A3-6)$$

Hence, substituting eqn. (A3-6) into eqn. (A3-5) yields

$$- \ln (1-\theta_B) = \exp\left(\frac{V_{sc}}{b}\right) + IC' \quad (A3-7)$$

The integration constant IC' is evaluated from the boundary conditions $\theta_B = 0$ and $V = V_{in}$ for $t=0$.

Then

$$IC' = - \exp\left(\frac{V_{in} - V_p}{b}\right) \quad (A3-8)$$

Combining eqns. (A3-7) and (A3-8) gives

$$- \ln(1-\theta_B) = \exp\left(\frac{V_{sc}}{b}\right) - \exp\left(\frac{V_{in} - V_p}{b}\right) \quad (A3-9)$$

Taking eqn. (4-8) in logarithmic form, substituting V_{sc} from eqn. (A3-2) and substituting $\ln(1-\theta_B)$ term from eqn. (A3-9), leads to

$$\ln i = \ln \frac{Qs}{b} + \frac{V_{sc}}{b} + \exp\left(\frac{V_{in} - V_p}{b}\right) - \exp\left(\frac{V_{sc}}{b}\right) \quad (A3-10)$$

Defining the initial potential V_{in} as a scaled potential, viz.

$$V_{sc,in} = V_{in} - V_p \quad (A3-11)$$

enables the current density, i , to be written in a general form

$$i = \frac{Qs}{b} \exp\left[\frac{V_{sc}}{b} + \exp\left(-\frac{V_{sc, in}}{b}\right) - \exp\left(-\frac{V_{sc}}{b}\right)\right] \quad (A3-12)$$

from which the pseudocapacitance C may be obtained

$$C = \frac{Q}{b} \exp\left[\frac{V_{sc}}{b} + \exp\left(-\frac{V_{sc, in}}{b}\right) - \exp\left(-\frac{V_{sc}}{b}\right)\right] \quad (A3-13)$$

This is seen to be a common function of the scaled potential for any value of s as is also the derivative of the above eqn. (A3-13):

$$\frac{dC}{dV_{sc}} = \frac{Q}{2} \exp\left[\frac{V_{sc}}{b} + \exp\left(-\frac{V_{sc, in}}{b}\right) - \exp\left(-\frac{V_{sc}}{b}\right)\right] \left[1 - \exp\left(-\frac{V_{sc}}{b}\right)\right] \quad (A3-14)$$

Hence all C - V profiles for reaction (I) under irreversible conditions have a common form.

A similar conclusion was reached by Laviron⁸⁰ proceeding in a different way.

CLAIMS TO ORIGINAL RESEARCH

1. The various types of kinetic behaviour which arise in a number of electrochemical surface reactions involving adsorbed species up to a monolayer in coverage have been simulated on a computer for conditions where the reaction is driven by a linear potential sweep. A general programme for solving the differential equations, which mathematically describe the electrochemical processes investigated, has been written using a simulation language "System/360 Continuous System Modeling Program-(S/360 CSMP)". A separate subroutine, which embodies the properties of a function generator, has also been developed using the FORTRAN language.
2. Simulations of current-potential profiles for a single step, 1-e electrochemical surface reaction under both reversible and irreversible conditions have been performed for cases where significant attractive or repulsive interactions arise between the adsorbed species at the electrode. The effects of reversing the sweep at various potentials, i.e., various coverages, especially when the process behaves irreversibly and is associated with significant positive or negative values of g , have been derived. Analytical derivations of characteristic parameters i_p , V_p and θ_p for irreversible conditions, derived previously by other workers only for Langmuir behaviour, have been made more general by extension to the case where adsorption follows the Temkin isotherm.

3. A method for distinguishing between the current-potential profiles for a simple 1-e surface process and for two surface processes involving parallel steps, when the electrochemical reactions involving the adsorbed species occur over the same potential region, has been developed. The technique used to distinguish the two processes involves the "kinetic relaxation" properties of the reaction. This method can be used if one of the adsorbed species behaves more "reversibly" than the other. The coverages by the two species involved can also be obtained.
4. Simulation calculations have also been applied to the case where a first-order chemical surface step precedes or follows a simple 1-e electrochemical process, thus giving rise to either a "ce" or an "ec" type of overall mechanism. The current-potential profiles have been shown to depend not only on the reduced sweep-rate s/k , but also on the ratio of the rate constants of the two steps. Comparison with results for the 1-e surface reaction has been made. Methods for determination of kinetic parameters and of the standard electrode potential values, E° , have been discussed and it has been shown that effects of holding of the potential, especially at the end of the sweep, provide information of considerable importance in characterizing this kind of mechanism.
5. Current-potential profiles for a three-step reaction mechanism under various sweep-rate conditions have been simulated. The three stages are represented by an irreversible dissociative chemisorption step producing two chemisorbed intermediates, followed by two

parallel electrochemical processes, one of which is assumed to be completely irreversible and the other reversible. The effect of varying the ratios of the initial coverages of the two chemisorbed species on the i - V profiles which result has been demonstrated. It was also shown that the current-potential profiles depend on the reduced sweep-rate s/k_3 (k_3 being the rate constant for the irreversible electrochemical step) as well as on the ratio k_1/k_3 (k_1 being the rate constant of the chemical step for the dissociative reaction at the surface). Methods for determining the kinetic parameters which are involved in some of the steps and the E° values have been described.

6. An exploratory mathematical treatment of the direct logarithmic growth law which experimentally characterizes growth of oxide films on metals has been given in terms of a place-exchange reaction. The potential dependence of the parameters in the rate equation describing the place-exchange process has been considered. It is also pointed out that the rate equation must be of zero-order in the pre-exponential terms and the rate of the place-exchange reaction should decrease exponentially with increasing quantity of deposited oxygen species which has undergone the rearrangement if a direct logarithmic law is to be obtained by integration of the rate equation.
7. Current-potential curves for various applied sweep-rates for the case where inhibition of a Faradaic process occurs by electro-deposition of a co-adsorbed species from a parallel reaction have been calculated. It is assumed in the calculations that the Faradaic

reaction occurs in two steps, the first being the rate determining electrochemical process and the second one is a fast chemical desorption reaction. Various procedures for determination of the rate constants and the standard electrode potential values have been considered and it was shown how the pertinent information may be obtained from the Tafel plots.

8. Simulations of the kinetic behaviour arising in the case of a nucleation-controlled mechanism where film formation occurs by growth from nuclei on the electrode surface have been made. The case of a simple 1-e electrochemical reaction proceeding by this mechanism under potentiodynamic and, for comparison, under potentiostatic conditions has been considered. The characteristic parameters such as i_p , V_p , θ_p and t_p , which arise from various assumed conditions have been derived analytically for all the cases. In these derivations, the statistical approach of Evans has been utilized. The kinetic behaviour of this type of process was then compared with that of the random 1-e surface process obeying either a Langmuir or Temkin type of isotherm and the distinguishing features of the two types of processes have been derived.
9. Features of i - V (potentiodynamic case) and i - t (potentiostatic case) profiles which can distinguish the nucleation-controlled mechanism for constant and varying number of nuclei as a function of time and potential have been discussed. The equations for the reversibility parameters, i.e., $i_{p,0}$ and $t_{p,0}$ for potentiostatic conditions and s_0 for potentiodynamic conditions, for both varying and constant number

of nuclei have also been derived and comparisons have been made. A general reduced form of the current-time transient, independent of arbitrary values of parameters of the process, has been derived.

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