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A.C. IMPEDANCE OF FARADAIC REACTIONS INVOLVING ELECTROSORBED INTERMEDIATES;

Part I: Kinetic Theory

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(Received:)

Abstract

The evaluation of the electrochemical adsorption behaviour of chemisorbed intermediates generated in a multi-step Faradaic reaction at appreciable net currents is important for understanding the reaction mechanism of the overall process involved. Measurement of a.c. impedance of the reaction at controlled potentials provides an important experimental route to the required information about the "overpotential-deposited" ad-atom species. Interpretation of the measurements requires, however, further examination.

Based on an extension of Armstrong's treatment, it is shown that interpretation of a.c. impedance measurements directly in terms of the components of an intuitively assumed equivalent circuit is rarely correct; only in the case of underpotential-deposition of an ad-species, where no continuous Faradaic currents pass, is such an approach satisfactory. Kinetic analysis is given for the behaviour of a multistep process with examples from the cathodic H₂ evolution reaction where electrochemical and H-recombination desorption pathways are involved. The kinetic analysis enables the steady-state adsorption pseudocapacitance C_φ for H to be evaluated as a function of overpotential. Its behaviour is clearly distinguishable from the quantity C_p commonly written as the pseudocapacitance element in the equivalent circuit for this type of reaction.

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INTRODUCTION

The a.c. impedance technique is widely used to study electrode processes.¹ Most of the experimental data obtained from such experiments are analysed in terms of an "equivalent circuit", an electrical circuit which is considered to model correctly the electrical behaviour of the electrode interface when its calculated impedance, as a function of frequency, agrees with the experimentally measured impedance behaviour. In the simplest, or "intuitive" method of analysis, it is assumed that the elements of the experimentally derived equivalent circuit may be identified with parameters of the electrical behaviour of the individual constituent steps of the reaction mechanism, viz. charge transfer resistances, pseudocapacitances and diffusional impedances.

A more rigorous method of analysis involves comparison of the experimentally measured impedance directly with that theoretically derived for an assumed reaction mechanism. If agreement is found, the adsorption parameters and the rate constants of the constituent steps of the mechanism can be readily calculated. The concept of an equivalent circuit is not a necessary part of this "kinetic" method of analysis, although the theoretical derivation can be used to assign acceptable equivalent circuits. The analysis shows that the significances of the equivalent circuit elements assumed in the "intuitive" method are rarely correct. In particular, it will be shown that the one-to-one assignment of resistances to individual reaction steps, as is commonly done, is not usually valid.

In this paper we discuss the significance of the equivalent circuit elements in relationship to the theory for a multi-step reaction with one adsorbed intermediate, without diffusion control. The treatment is an extension of Armstrong's

kinetic theory for the two-step case.² Although theoretical treatments have been given for generalized mechanisms, of which this is a specific case,³ the consequences for this case and the derivation of equivalent circuits have not been pursued. After deriving acceptable equivalent circuits, the physical significance of the constituent resistors, capacitors and inductors is discussed. We also examine the concept of adsorption pseudocapacitance and its relationship to the equivalent circuit elements, and introduce a useful new quantity, the a.c. pseudocapacitance. While some of the points presented here have been indicated previously in the literature, as cited, it is useful to mention them again as part of an integrated discussion of the a.c. method for study of surface reactions.

A mechanism was chosen in which a single electroadsorbed intermediate is formed, as in the hydrogen evolution reaction (h.e.r.). In the paper which follows⁴, an experimental a.c. impedance study of the h.e.r. at platinum electrodes is described and analysed using the methods given here. We therefore apply the theory to the mechanism of the h.e.r., considering the reaction steps of proton discharge with electroadsorption (Volmer reaction, eqn. (1)), electrochemical desorption (Horiuti reaction, eqn. (2)) and H recombination (Tafel reaction, eqn. (3)). The recombination reaction is an important component of the h.e.r. at Pt, but does not seem to have been incorporated into previous impedance analyses, except those of Gerischer and Mehl⁵ and Brug et al⁶.



The analogous bromine evolution reaction at vitreous carbon electrodes in acetonitrile has also been studied in this laboratory and the results have been analysed by the methods given in this paper.⁷

The h.e.r. is perhaps the most widely studied electrochemical reaction. Although the a.c. impedance method has been used to study the upd of hydrogen on platinum^{8,9,10,11}, there are surprisingly few impedance studies of the h.e.r. in the overpotential region. Gerischer and Mehl⁵ made impedance studies of the h.e.r. at mercury, silver and copper electrodes but the theoretical treatment presented there applies only to the Tafel region. This restriction means that the important potential region in which the surface coverage by the electroactive intermediate is changing appreciably with potential could not be considered. Also, the experimental results were not fitted by the theoretical model they proposed. Brug et al.⁶ made a detailed experimental study of the h.e.r. at Au which showed no evidence of an adsorption capacitance associated with H and gave a theoretical treatment for several limiting cases. This paper was the first to treat theoretically the impedance in the potential region where the coverage θ is changing.

Other experimental impedance studies of the h.e.r. have been reported by Armstrong and Bell¹², Breiter Knorr and Yökl¹¹, Durand¹³, Frumkin et al¹⁴ and Sluyters-Rehbach and Sluyters¹⁵, as discussed in more detail in Part II. However, these papers do not contain any further theoretical development relevant to the present work. A series of papers by Epelboin and co-workers¹⁶⁻¹⁹ concerning experimental and theoretical aspects of the dissolution of the iron electrode is relevant insofar as one of the mechanisms discussed is similar to eqns. (1) and (2), but a recombination reaction was not considered. The theory here is extended to the case of two adsorbed intermediates in Part III²⁰ where it is applied to the h.e.r. at Ni-Mo-Cd alloys involving sorbed as well as adsorbed H.

THEORETICAL TREATMENT AND DISCUSSION

1. General Derivation and Equivalent Circuits

In this section we derive equivalent circuits for any mechanism with one adsorbed intermediate, in which diffusion of participating species is not rate-

limiting. In the following equations, $r_0 = i/F$ is the net rate (in $\text{mol cm}^{-2} \text{s}^{-1}$) of production (r_0 positive) or consumption (r_0 negative) of electrons, $r_1 = (q_1/F)(d\theta/dt)$ the net rate of production of the adsorbed species, θ is the fractional surface coverage of the adsorbed intermediate and q_1 is the charge required for deposition of the ad-species to complete coverage. The international sign convention is used, i.e. cathodic currents are taken as negative.

The rates of production of electrons or adsorbed intermediate have contributions from several steps in the mechanism. For example, for the h.e.r. proceeding with the mechanism represented by eqns. (1) - (3), r_0 and r_1 are given by eqns. (23) and (24), developed later.

When there is sinusoidal modulation of potential at frequency $\omega/2\pi$:*

$$E = E_{SS} + E_{ac} \cos(j\omega t + \theta_E) = E_{SS} + \text{Re}[\tilde{E} \exp(j\omega t)] \quad (4)$$

$$\theta = \theta_{SS} + \theta_{ac} \cos(j\omega t + \theta_\theta) = \theta_{SS} + \text{Re}[\tilde{\theta} \exp(j\omega t)] \quad (5)$$

$$i = i_{SS} + i_{ac} \cos(j\omega t + \theta_i) = i_{SS} + \text{Re}[\tilde{i} \exp(j\omega t)] \quad (6)$$

Equation (4) gives the applied potential, consisting of the d.c. or steady-state (ss) potential E_{SS} and the small amplitude sinusoidal component of magnitude E_{ac} and phase θ_E . $\tilde{E} = E_{ac} \exp(j\theta_E)$ is the complex quantity characterising the a.c. component. Both θ (eqn. (5)) and i (eqn. (6)) will also vary sinusoidally but with different phase and amplitude (contained in \tilde{i} and $\tilde{\theta}$). For small perturbation from the steady-state, the rates may be expanded in Taylor series form, neglecting second and higher order terms (eqns. (7) and (8)):

* These equations, and those following up to (15b) are related to those in Armstrong's treatment² but they are written here (in a generalized form with somewhat different notation) in order that the subsequent analysis and conclusions given in this paper regarding equivalent circuits may be conveniently followed.

$$i/F = r_0 = r_{0,ss} + (\partial r_0 / \partial E)_\theta (E - E_{ss}) + (\partial r_0 / \partial \theta)_E (\theta - \theta_{ss}) \quad (7)$$

$$(q_1/F) \frac{d\theta}{dt} = r_1 = r_{1,ss} + (\partial r_1 / \partial E)_\theta (E - E_{ss}) + (\partial r_1 / \partial \theta)_E (\theta - \theta_{ss}) \quad (8)$$

Here $E - E_{ss}$ and $\theta - \theta_{ss}$ are the deviations from the ss values of E and θ , respectively, caused by the a.c. modulation.

To simplify the treatment which follows, it is convenient to define three parameters A , B and C as in eqns. (9a,b,c). $\tilde{\theta}/\tilde{E}$ (eqn. (10) may then be obtained by substituting eqns. (4) and (5) into eqn. (8) (note that $r_{1,ss} = 0$). The Faradaic admittance, $\tilde{Y}_f = \tilde{i}/\tilde{E}$ (eqn. 11), may finally be obtained by using eqns. (4) - (7) and (9). Several forms of this equation are given: (11a) is the simplest, (11b) conforms closely with Armstrong's notation and (11c) - (11f) are written to show that the equation is the same as those for the equivalent circuits shown in Fig. 1. The capacitive circuit, Fig. 1(a), has been given by Armstrong,² the only difference from the presentation here being that his circuit elements took into account only two reaction steps. Both the capacitive and inductive circuits (Figs. 1a,b) have been used by Epelboin and co-workers.¹⁷

It is convenient to define the following:

$$A = F(\partial r_0 / \partial E)_\theta \quad (9a)$$

$$B = (F^2/q_1) (\partial r_0 / \partial \theta)_E \cdot (\partial r_1 / \partial E)_\theta \quad (9b)$$

$$C = -(F/q_1) (\partial r_1 / \partial \theta)_E \quad (9c)$$

$$\tilde{\theta}/\tilde{E} = (\partial r_1 / \partial E)_\theta / [j\omega q_1/F + (\partial r_1 / \partial \theta)_E] \quad (10)$$

$$\tilde{Y}_f = A + B / (j\omega + C) \quad (11a)$$

$$= 1/R_\infty + 1/R_0(1 + j\omega\tau) \quad (11b)$$

$$= [R_\infty + 1/(\frac{1}{R_p} + j\omega C_p)]^{-1} \quad (11c)$$

$$= 1/R_\infty + 1/(R_0 + j\omega L_s) \quad (11d)$$

$$= 1/R_f + 1/(R_s + 1/j\omega C_s) \quad (11e)$$

$$= [R_f + (1/R_L + 1/j\omega L_p)^{-1}]^{-1} \quad (11f)$$

where $R_\infty = 1/A$; $\tau = 1/C$; $R_O = C/B$; $R_f = C/(CA + B)$; $R_p = -B/A(CA + B)$; $C_p = -A^2/B$; $L_s = 1/B$; $C_s = -B/C^2$; $R_s = -R_O = -C/B$; $R_L = -R_p = B/A(CA + B)$ and $L_p = B/(CA + B)^2$. It is clear from eqns. (9) - (11) that the parameters A, B and C have a simpler meaning than the equivalent circuit elements, which are much more complex functions of the kinetic parameters.

It is possible that adsorption of the intermediate might alter the charge of the double-layer (additionally to the faradaic contribution) leading to a θ dependence of C_{dl} .¹⁶ However, in this paper, we assume that this effect is small and therefore make the usual simplification concerning the additivity of the Faradaic and double-layer charging currents, i.e. the admittance of the double-layer capacitance is added to Y_f and the total interfacial impedance is then given by:

$$\tilde{Z} = 1/(\tilde{Y}_f + j\omega C_{dl}) \quad (12)$$

The possible shapes of this function when plotted in the complex plane have been given by Armstrong²: they approximate to two semicircles either both above the real axis or one above and one below. For certain limiting conditions, these may appear merged into one semicircle as is sometimes found experimentally (Part II). It should be noted that some of the shapes given by Armstrong may not necessarily arise for a given mechanism because the parameters of eqns. (11) are not independent but are related through the details of the specific mechanism. We have only observed shapes like those of Fig. 2 in the case of the h.e.r. (see below).

2. Significance of parameters of eqns. (11) determining the equivalent circuit elements

Although all the forms of eqn. (11) are mathematically equivalent, all resistances, capacitances and inductances in a real circuit have positive values.

This restriction is not implicit in eqn. (11), so that the possible signs of the parameters require discussion.

These signs depend on the signs of the partial derivatives of the rates with respect to θ and E . At constant θ , the rate of each electron transfer step increases with increasing overpotential, i.e. $(\partial r_0 / \partial E)_\theta$ is therefore always positive, leading to a positive A (eqn. (9a)). The rate of a step which produces adsorbate generally decreases with increasing θ , at constant E , because the back reaction is promoted and the forward reaction inhibited. This leads to C being always positive (eqn. 9c). Consequently, for most cases of interest, both A and C are positive, but B may be of either sign.

From eqn. (11), it is seen that, for negative B , all elements of the capacitive (Armstrong) circuit (Fig. 1a) are positive, while for positive B all elements of the inductive circuits (Figs. 1b, d) are also positive. For the series capacitive circuit, Fig. 1c, at least one of the elements will be negative, regardless of the sign of B . The "natural" equivalent circuit could be taken as the one with all elements positive, the usual convention adopted (cf. ref. 17, with Q instead of B). This choice has the difficulty that different circuits may have to be chosen at different d.c. potentials, if B changes sign¹⁷. Alternatively, recognizing that it is the kinetic scheme that actually describes the reactions, each of the forms of eqn. (11) might be considered equally suitable, whatever the signs of the parameters. We take the view that, for the purposes of analysing data, whichever circuit is most convenient may be chosen, though the data are probably most conveniently analysed in terms of A , B and C without adopting any equivalent circuit. However, it is useful to have an equivalent circuit whose elements correspond to something of mechanistic significance. We show below that, in this sense, the inductive circuit, Fig. 1b, is to be preferred, even though the elements may be negative for negative B .

The form of eqn. (11) is derived quite generally, without regard to the actual potential-dependence of r_0 or r_1 , or the form of the adsorption isotherm of the intermediate species. Consequently, any reaction mechanism with one adsorbed intermediate and without diffusion control will give rise to an impedance with a frequency dispersion governed by eqn. (15) and should therefore be analysed in terms of A, B and C. If the data are analysed in terms of an equivalent circuit, only those of figure 1 are acceptable, since they follow directly from the kinetics.

Other equivalent circuits which do not conform to eqn. (11) will not provide a suitable basis for treating the data for reaction mechanisms with one adsorbed intermediate, i.e. we are not free to assume arbitrarily a form for the equivalent circuit. This conclusion is implicit in the generalized theories given by several authors^{1,3}, where the general formulation of the impedance function is given without detailed reference to implied equivalent circuits. Quite generally, there may be several equivalent circuits for the same mechanism but the equations describing their frequency dispersion behaviour will simply be different forms of the same equation, in this case eqn. (11). Consequently, at each d.c. potential, there should be some set of parameter values which allows eqn. (11) to be fitted to the experimental data; a misfit implies that the reaction does not have a single-adsorbate mechanism without diffusion control.

However, a correct fit with one of the acceptable equivalent circuits of eqn. (11), is seen to be insufficient to be diagnostic of the specific mechanism. For example, suppose it is found that, at each d.c. potential studied, the data fit the behaviour expected for one of the equivalent circuits given in Fig. 1. It is not possible to conclude from this alone whether or not the recombination step, say, should be included in the reaction mechanism. If the data do fit

eqn. (11), but the detailed potential-dependences of the parameters do not match those predicted for the specific reaction mechanism, then agreement may be obtained by altering the specific mechanism. The term specific mechanism is used here to mean a proposed series of steps, such as eqns. (1) - (3), with associated assigned rate constants and isotherm parameters.

It is to be noted that the equivalent circuit expected on intuitive grounds may sometimes be incorrect. In the present case, the circuit of Fig. 1a is often proposed with the interpretation that R_{∞} is the charge-transfer resistance of the electrosorption step, R_p is the charge-transfer resistance of the electro-desorption and/or recombination steps and C_p is the pseudocapacitance of the adsorbed species.²¹ In a recent paper, R_{∞} and R_p have instead been assigned to the "fast" and "slow" steps of the mechanism²². However, it is clear from the above derivation, that R_{∞} and R_p are each properties of two or more steps in the reaction, and therefore the above assignments cannot be justified. Additionally, it will be shown below that C_p may not be identified with what is usually called the adsorption pseudocapacitance^{23,24}, but is, however, related to it in a rather complicated way.

3. Significance of Parameters

(i) The parameter τ

As noted by Armstrong², τ is a time constant which measures how rapidly θ relaxes to its new value after the potential is changed. This has a quite precise meaning in the case where the rates are linear in θ , such as for the h.e.r. under Langmuir conditions with a negligible recombination rate. In this case, if the potential is stepped to a new potential, E_{ss} , then θ relaxes exponentially to its final value with a time constant τ (Fig. 3), the same value of τ which would be obtained in an a.c. impedance experiment at an applied d.c. potential E_{ss} .

(This may be shown by solving the differential equation for constant potential conditions.) In more complex cases, such as the h.e.r. with recombination considered, the relaxation will not be exponential, though non-rigorously a similar significance may be attached to τ . The time constant τ is equal to the time constants of the series branches of the circuits of Figs. 1b and 1c ($\tau = L_S/R_0 = C_S R_S$) but is not simply related to the elements of the other equivalent circuits.

(ii) Pseudocapacitance and Related Quantities

The steady-state pseudocapacitance, C_ϕ , the equivalent circuit element, C_p , and $q_1 (\bar{\theta}/\bar{E})$ all have the dimensions of capacitance. We discuss these in turn. In order to calculate the adsorption pseudocapacitance, C_ϕ , the steady-state value of θ at any d.c. potential, E_{SS} , is first found²³ by setting the r_1 equal to zero and solving for θ as a function of potential (Fig. 3). Differentiation of this function and multiplication by q_1 gives the quantity C_ϕ called the pseudocapacitance by most authors (Fig. 3). Extensive discussion of the C_ϕ function has been given in several papers by Conway and Gileadi^{23,25} for equilibrium and ss conditions.

Since r_1 is zero in every steady-state, its derivative with E_{SS} is also everywhere zero (eqn. (18)), leading to an alternative formula for the steady-state pseudocapacitance*, C_ϕ :

$$0 = dr_1/dE_{SS} = (\partial r_1/\partial \theta)_E d\theta_{SS}/dE_{SS} + (\partial r_1/\partial E)_\theta \quad (13)$$

$$C_\phi \equiv -q_1 d\theta_{SS}/dE_{SS} = +q_1 (\partial r_1/\partial E)_\theta / (\partial r_1/\partial \theta)_E \quad (14)$$

Because the derivative $(\partial r_1/\partial E)_\theta$ appears in combination with another derivative in B (eqn. (9b)), the pseudocapacitance at a given E cannot be obtained directly from the impedance parameters at this potential. It can, of course, be calculated from the rate constants^{23,25} once these are obtained from a full analysis of the potential-dependence of the impedance parameters. This latter method has the disadvantage that a specific reaction scheme must be assumed.

* C_ϕ is defined here as the negative derivative in order for C_ϕ to be positive for the h.e.r.

It should be noted that, since the coverage θ at a given potential depends on the potential programme applied to the interface, the quantity $q_1 d\theta/dE$ is not uniquely specified. For example, it has different values in a cyclic-voltammetry or an a.c. experiment from that for a steady-state current-potential measurement. The above definition of C_ϕ as derivative of the steady-state θ -E curve is the one used by several authors, although different quantities* have also been defined as pseudocapacitance in the literature, e.g. peak current divided by sweep-rate in cyclic-voltammetry or the value of a capacitance in an experimentally-determined equivalent circuit.

The complex quantity, $q_1 \tilde{\theta}/\tilde{E}$ (eqn. 15), measures how the sinusoidal variation of coverage by the adsorbed intermediate (expressed as equivalent charge) depends on the sinusoidal changes of the potential, analogously to the way admittance measures the dependence of a.c. current on a.c. potential. We shall call this quantity, which has the dimensions of capacitance, the "a.c. pseudo-capacitance", \tilde{C}_{ac} . Its significance does not seem to have been recognized previously. Thus:

$$\tilde{C}_{ac} = q_1 \tilde{\theta}/\tilde{E} = q_1 (\partial r_1 / \partial E)_\theta / [j\omega q_1 / F + (\partial r_1 / \partial \theta)_E] \quad (15)$$

with amplitude

$$|\tilde{C}_{ac}| = q_1 |(\partial r_1 / \partial E)_\theta| / [\omega^2 q_1^2 / F^2 + (\partial r_1 / \partial \theta)_E^2]^{1/2} \quad (16)$$

In the terminology of circuit theory, a pure capacitance is one where the current leads the voltage by a phase-angle of 90° or equivalently the charge on the capacitor plates is exactly in-phase with the potential across the plates at all frequencies. The sinusoidal variation of the charge stored as adsorbate is not in-phase with the sinusoidal changes in potential except at zero frequency. Only then, in the steady-state, can changes in charge keep up with changes in potential. At higher frequencies, a phase difference develops of course, and less amplitude of charge variation is obtained for the same potential amplitude

* The relationship between C quantities determined by a.c., d.c. and potential-sweep methods was treated by Conway, Gileadi and Kozłowska in an earlier paper²⁸.

(eqn. (16)) because of the slowness of the reaction. Accordingly a complex quantity (\tilde{C}_{ac}) describes the variation of amplitude and phase of adsorbate charge as a function of frequency (Fig. 3). In the limit of zero frequency, \tilde{C}_{ac} becomes the pure capacitance^{25,26}, C_ϕ , as may be seen by comparing eqns. (14) and (15).

The third quantity with dimensions of capacitance, C_p , (eqn. (17)) may also be compared with the steady-state pseudocapacitance (eqn. (14)) but it is seen that these two quantities are not, in general, equal. C_p is a pure capacitance and, in view of the preceding discussion, cannot be a true measure of the variation of adsorbed charge with potential under a.c. conditions. That is, the charge on its "plates" is not the same as the charge residing Faradaically as adsorbed intermediate on the electrode in an a.c. experiment. Rather, C_p results from the conventional requirement that an equivalent circuit must contain only elements whose values are real and frequency-independent i.e. pure capacitors, resistors and inductors. (The Warburg impedance is an exception to this rule). C_p appears in combination with the resistor R_p so that the combination correctly models the phase delay of the reaction scheme. It is not therefore to be expected that a definite physical significance can be ascribed to it. In the case of the h.e.r., however, the behaviour of C_p is found to be surprisingly similar to that of C_ϕ over a limited potential range in the absence of recombination (see below and Fig. 5). We therefore seek criteria for the similarity of these two functions, writing C_p as

$$C_p = -A^2/B = -q_1 [(\partial r_0 / \partial E)_\theta]^2 / [(\partial r_0 / \partial \theta)_E (\partial r_1 / \partial E)_\theta] \quad (17)$$

Comparison of eqns. (14) and (17) shows that they will be equivalent if $-r_0$ and r_1 are identical functions of θ and E to within an additive constant. (Other more complex functions which lead to equivalence are not considered here because they are unlikely to be physically reasonable.) The simplest case when C_p is equal to C_ϕ is with $-r_0 = r_1 = v_1$, i.e. where the adsorbate is formed and removed

with accompanying electron transfer in one step only. This is the case of underpotential deposition of hydrogen or other species. Mathematically, this may be considered a special case of the h.e.r. with $v_2 = v_3 = 0$, although the adsorbed species in underpotential deposition (UPD) are probably in a different state from the electro-active (OPD) adsorbate species in the overpotential region.

In this UPD case, the capacitative quantities, C_p and C_ϕ are identical. Furthermore, since R_p (eqns. 11 and 9) is infinite, the equivalent circuit of Fig. 1a reduces precisely to that of Fig. 4. If the specific rate expression for UPD (following the Langmuir isotherm with $\beta = 0.5$, eqn. (18)) is inserted into eqns. (11) and (9), the potential dependences of the circuit elements of Fig. 4 accord precisely with the intuitive expectations for a simple charge-transfer resistance and an adsorption pseudocapacitance (eqns. (19) and (20)). This circuit has been widely used in the analysis of UPD data by Breiter and others^{10,8}, and theoretical justification has been given by Dolin and Ershler⁸.

The question arises as to why the intuitive notion of the role of pseudocapacitance in the equivalent circuit is in accord with the mathematical predictions in the case of UPD but not in the more general OPD case. The explanation is that it is only in UPD that every electron passed produces an adsorbate molecule, so that the Faradaic charge passed, q , is identical with the charge stored as adsorbate, $q_1\theta$ (eqn. (21)). There are no "leakage" reactions such as eqns. (2) or (3), corresponding to overall product formation, to upset this equality and lead to the kinds of difference calculated by Gileadi and Conway^{23,25} for quasi-equilibrium and steady-state/OPD C_ϕ quantities. Summarizing, for UPD only (with $\beta = 0.5$):

$$r_o = r_1 = k[(1-\theta)\exp(\bar{0.5FE/RT}) - \exp(0.5FE/RT)] \quad (18)$$

$$R_\infty = (RT/0.5kF^2)\cosh(0.5FE/RT) \quad (19)$$

$$C_p \equiv C_{ac} (\omega=0) \equiv C_\phi = (Fq_1/4RT)\cosh^{-2}(0.5FE/RT) \quad (20)$$

and

$$i = dq/dt = q_1 d\theta/dt \quad (21)$$

Although $r_0 = -r_1$ is only strictly true for UPD, it can be approximately true for more complex mechanisms if the adsorbed species is formed in an almost reversible electron-transfer step and other following steps involving charge-transfer or adsorbate reaction are rate-determining (quasi-equilibrium assumption). For the h.e.r., this will arise when electrodesorption and recombination have much smaller rate constants than that for electrosorption. In potential regions where this applies, C_p and C_ϕ will be similar. This condition may not hold at potentials in the Tafel region, because there the electron-transfer step producing the electrosorbed species is polarized strongly in one direction.

(iii) Resistances

As usual in impedance analysis, the impedance reduces to a charge-transfer resistance, R_∞ , in the high-frequency limit and a faradaic resistance, R_f , in the low-frequency (d.c.) limit. We note that r_0 is the sum of the rates of the various charge-transfer steps. Consequently $1/R_\infty$ is the sum of similar reciprocal resistances $1/R_{\infty 1}$, $1/R_{\infty 2}$ etc. for each charge-transfer step. It depends on the rates of chemical steps only indirectly, through the dependence on θ_{ss} in these steps.

The faradaic admittance may be written in terms of C_{ac} (eqn. (22)):

$$\tilde{Y}_f = 1/R_\infty + F/q_1 (\partial r_0 / \partial \theta)_E C_{ac} \quad (22)$$

In this form, the two terms may be interpreted as follows: The first term, $1/R_\infty = (\partial i_{ss} / \partial E)_\theta$ is frequency independent and determines the instantaneous amount by which the current increases when the potential is perturbed without allowing θ to change. The second term represents the contribution to the admittance from the relaxation of coverage following the potential perturbation. It is frequency dependent because of the slowness of the reactions.

In the limit of zero frequency, C_{ac} becomes C_{ϕ} and the second (relaxation) term of eqn. (22) becomes $1/R_0$. R_0 is therefore associated with relaxation of coverage and is the energy-dissipating element associated with this process. This discussion indicates the significance of the sign of B (eqn. 9b), which is the same as the sign of the relaxation term: B is negative if a small increase in the magnitude of the overpotential (whether cathodic or anodic) leads to relaxation associated with a current that is opposite to that flowing before the change.

(iv) Inductances

The inductances L_s and L_p have a similar significance to C_p , i.e. they are ideal components which arise in combination with resistors (R_0 or R_L) in order to model the phase delay of the coverage relaxation, which is not 90° . When the current in an inductor changes, an opposing induced emf is set up. Conversely, we consider a negative inductor as a circuit element in which the induced emf is in the same direction as the current change. With this in mind, a correspondence is expected between the terms of eqn. (22) and the parts of the series-inductive circuit, Fig. 1c. Thus, the first term, $1/R_0$, is one parallel arm of the circuit and is associated with the charge-transfer part of the current response which occurs without change in θ . The second term, containing the a.c. pseudocapacitance, is the $R_s L_s$ arm of the circuit and is associated with the additional part of the current response which occurs as θ changes. This shows why, for negative B , the inductive equivalent circuit is a "natural" one, i.e. ^{it} has positive elements: it is in this case that the θ relaxation current response opposes that due to charge transfer at constant coverage. This circuit is to be preferred even in the case of positive B , where the inductance is negative, because similar mechanistic significance can be assigned to its elements, even though the circuit cannot be built from real components.

AN EXAMPLE - THE HYDROGEN EVOLUTION REACTION

The above discussion is illustrated here for the mechanism of the h.e.r. (eqns. (1) - (3)) which is readily treated by incorporating eqns. (23) and (24) for r_0 and r_1 into the steps of the derivation above, where v_1 , v_2 and v_3 denote the net rates of the respective steps represented in eqns. (1) - (3) in the directions written. v_3 is defined as the rate of H_2 production in step 3, or half the rate of consumption of H, expressed as θ , in that step; hence the coefficient 2 appears in eqn. (24). Explicit expressions for v_1 , v_2 and v_3 are given in eqns. (25a-c) below. The Langmuir isotherm and β values of 0.5 have been assumed, and the concentrations of H^+ and H_2 have been absorbed into the rate constants:

$$r_0 = -(v_1 + v_2) \tag{23}$$

$$r_1 = v_1 - v_2 - 2v_3 \tag{24}$$

with

$$v_1 = k_1(1-\theta)\exp(0.5FE/RT) - k_{-1}\theta \exp(0.5FE/RT) \tag{25a}$$

$$v_2 = k_2\theta \exp(0.5FE/RT) - k_{-2}(1-\theta)\exp(0.5FE/RT) \tag{25b}$$

$$v_3 = k_3\theta^2 - k_{-3}(1-\theta)^2 \tag{25c}$$

and

$$k_1k_2/k_{-1}k_{-2} = k_1^2k_3/k_{-1}^2k_{-3} = 1 \tag{26}$$

If the usual overpotential scale is chosen for the rate constants, then they are not all independent but must be related through the equilibrium constant for the overall reaction (eqn. 26). The partial derivatives of eqns. (25a-c) are readily evaluated and ^{when} inserted into eqns. (23), (24), (9) and (11) give the equivalent circuit parameters as functions of overpotential. The partial derivatives appear in the Taylor series expansion around the steady-state condition and must therefore be evaluated using the steady-state θ . This may be obtained by setting eqn. (24) to zero and solving for θ . Since these various algebraic

manipulations are best evaluated as successive lines of a computer program, we do not give the resulting complex expressions here.

The potential dependences of the equivalent circuit elements, derived in this way, are depicted graphically in Fig. 5, for three cases of interest:

1) where the rate constants of the first step are much less than those of the second step and where recombination is negligible, as is the case for the h.e.r. on Au^{c} , Hg or other metals not catalytic for the h.e.r.

2) where the rate constant of the first step is larger than that of either the electrodesorption or the recombination step which compete to remove the adsorbate, as is the case for the h.e.r. at Pt (Part II). The rate constants for recombination have been deliberately chosen to be larger than those found experimentally in order to provide a clear comparison between the behaviour with and without recombination.

3) as for case 2) but without recombination.

We first note that most of the quantities plotted in Fig. 5 increase exponentially (Tafel behaviour) or decrease exponentially at high overpotentials. Increasing the degree of recombination increases the potential range over which non-exponential behaviour is observed, corresponding to the range over which appreciable changes in θ_{SS} occur. We note that the potential-dependent electrodesorption rate must always exceed the recombination rate at high enough potentials, and then exponential behaviour will be observed. The most striking effect of recombination is observed in the case of the parameters B , L_s and R_0 where a flat region is observed to high potentials in the presence of recombination, instead of the exponential behaviour when recombination is absent. The flat region arises even when other circuit elements show exponential behaviour, for the same set of rate constants. The parameters B , L_s and R_0 are therefore the most diagnostic for participation of recombination.

In case 1), as at Hg, both θ and C_ϕ are small in the experimentally accessible overpotential region, as expected. Here θ decreases as the reaction is driven further in the forward direction, so that C_ϕ is negative in this case.

Fig. 5 shows that the total Faradaic resistance, R_f , has a maximum and then falls exponentially toward zero on either side at potentials in the Tafel region. R_f is the reciprocal of the slope of the steady-state i - E curve and accordingly becomes small at high overpotentials. In the Tafel region, θ is not changing appreciably with potential and the relaxation term will contribute negligibly to the total Faradaic resistance. Fig. 5 also shows that, R_p and $1/R_0$ are small at high overpotentials. The maxima of R_0 , R_∞ and R_f do not, in general, appear at the same potential and there is no simple relationship between the peak potentials. The values of R_f and R_∞ are largest for the case where the rate constants for the first step are low and determine the rate. The plots show that participation of recombination affects the value of R_∞ , thus verifying that this resistance cannot be associated with only the first step of the mechanism, as discussed earlier.

The quantities τ , C_ϕ and C_p show similar peaks, typically within 0.2 V of the reversible potential (as found experimentally, Part II and in ref. 27 for Ni) but without any simple relationship arising between the peak potentials. Unlike τ and C_ϕ , C_p becomes very large at high overpotentials, as we observed experimentally for the bromine evolution reaction at vitreous carbon in CH_3CN ⁷. C_p superficially resembles the sum of the peaked C_ϕ function and a superimposed larger cosh function, although we have been unable mathematically to decompose C_p in such a simple way. The height of the peaked component is largely determined by the monolayer charge, q_1 , but the peak is sometimes obscured by the much larger cosh component (Fig. 5).

In cases where H recombination is unimportant and $\beta = 0.5$, the maxima of C_ϕ and τ are at the same potential (eqn. (27)), as may be readily shown by differentiation. The higher the potential of this peak, the smaller is K_1 , the equilibrium constant for the first step:

$$\eta_{\tau, \max} = \eta_{C_\phi, \max} = \frac{RT}{F} \ln [(k_1 + k_2)/(k_{-1} + k_{-2})] \quad (27)$$

Finally, we remark that although B was allowed to be positive in the theoretical section above, a set of rate constants for the h.e.r. could not be found that leads to positive B in our simulations, nor have we found an example in the experimental study of the h.e.r. at Pt (Part II).

CONCLUSIONS

The theoretical representation of the impedance of a multi-step mechanism with a single adsorbate, in the absence of diffusion control, can be made in terms of four possible equivalent circuits. Although there is no a priori reason for preferring one over another for the purposes of data analysis, it is convenient to be able to attach some mechanistic significance to the elements of the circuit chosen. It is shown that the usual interpretation of the elements of the capacitive circuit, Fig. 1a, is incorrect: thus it is not possible to associate individual steps of the reaction mechanism with individual resistances in this circuit, nor does the capacitance (C_p) correspond with the steady-state adsorption pseudocapacitance (C_ϕ). However, in the special case of underpotential adsorption, the resistance and capacitance of the circuit of Fig. 4 do, in fact, have their usual significance.

The equivalent circuit whose elements are most readily given mechanistic significance is the inductive circuit of Fig. 1b. The three parallel arms of this circuit correspond to the two terms of the Faradaic admittance and the admittance associated with the double-layer capacitance. The arm containing R_∞

is associated with the part of the current response which occurs without change of coverage when the potential is changed. This part is purely resistive because the reaction can respond immediately to potential changes if the coverage does not have to change. The arm containing R_0 and L_S is associated with the part of the current response which occurs as θ changes. This coverage relaxation part of the Faradaic admittance is related to the a.c. pseudocapacitance, which is a function of frequency and reduces to the steady-state pseudocapacitance in the limit of zero frequency.

An emf is induced in an inductor to oppose the current change occurring and this corresponds to the coverage relaxation part of the Faradaic process opposing the coverage-independent charge-transfer part (for positive B). The converse is true for a negative inductor, corresponding to negative B. The series resistor, R_0 , serves to modify the phase delay of the current to the value required by the reaction scheme, instead of the 90° provided by the inductor alone.

The potential dependences of the equivalent circuit parameters have been given for the case of the h.e.r., and the effect of participation of significant H recombination on these parameters has been evaluated.

ACKNOWLEDGEMENTS

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Captions to Figures (Harrington and Conway)

Fig. 1 Equivalent circuits for single-adsorbate mechanisms without diffusion control. (Definitions of the symbols are given in eqn. (11). Circuits (a) and (d), and (b) and (c), can be considered to belong together.)

Fig. 2 Impedance curves for the h.e.r.: a) Bode plot; b) complex-plane plot (with frequencies in Hz); $C_{d1} = 25 \mu\text{F cm}^{-2}$; $q_1 = 210 \mu\text{C cm}^{-2}$.

Curve A: $k_1 = 10^{-9}$, $k_{-1} = 10^{-7}$; $k_2 = 10^{-10}$; $k_{-2} = 10^{-12}$; $k_3 = k_{-3} = 0 \text{ mol cm}^{-2} \text{ s}^{-1}$.

Curve B: $k_1 = 10^{-9}$; $k_{-1} = 10^{-7}$; $k_2 = 10^{-10}$; $k_{-2} = 10^{-12}$; $k_3 = 10^{-7}$; $k_{-3} = 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$.

Fig. 3 Coverage and capacitance functions for the h.e.r.

a) Steady-state pseudocapacitance, C_ϕ ; circuit element, C_p . Steady-state coverage, θ_{ss} ; $k_1 = 10^{-9}$, $k_{-1} = 10^{-7}$, $k_2 = 10^{-12}$, $k_3 = k_{-3} = 0 \text{ mol cm}^{-2} \text{ s}^{-1}$; $q_1 = 210 \mu\text{C cm}^{-2}$.

b) Magnitude of the a.c. pseudocapacitance as a function of overpotential and frequency.

$k_1 = 10^{-9}$, $k_{-1} = 10^{-7}$, $k_2 = 10^{-10}$, $k_{-2} = 10^{-12}$, $k_3 = 10^{-7}$, $k_{-3} = 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$; $q_1 = 210 \mu\text{C cm}^{-2}$.

Fig. 4 Equivalent circuit for underpotential deposition of hydrogen.

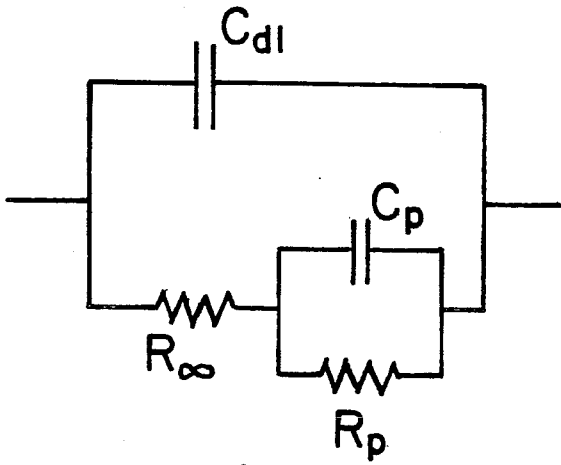
Fig. 5 Potential-dependency of equivalent-circuit elements and other parameters for the h.e.r.:

case (i) $k_1 = 10^{-15}$, $k_{-1} = 10^{-13}$, $k_2 = 10^{-10}$, $k_{-2} = 10^{-12}$, $k_3 = k_{-3} = 0 \text{ mol cm}^{-2} \text{ s}^{-1}$;

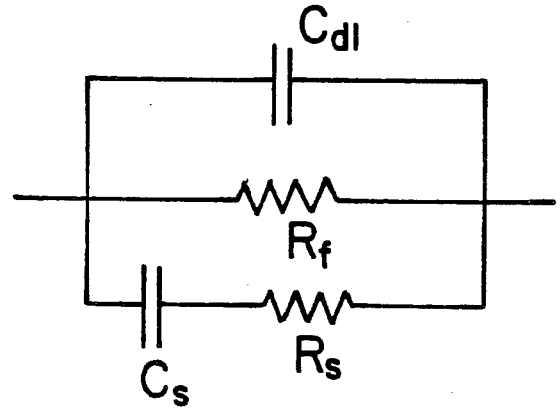
case (ii) $k_1 = 10^{-9}$, $k_{-1} = 10^{-7}$, $k_2 = 10^{-10}$, $k_{-2} = 10^{-12}$, $k_3 = 10^{-7}$, $k_{-3} = 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$;

case (iii) $k_1 = 10^{-9}$, $k_{-1} = 10^{-7}$, $k_2 = 10^{-10}$, $k_{-2} = 10^{-12}$, $k_3 = k_{-3} = 0 \text{ mol cm}^{-2} \text{ s}^{-1}$.

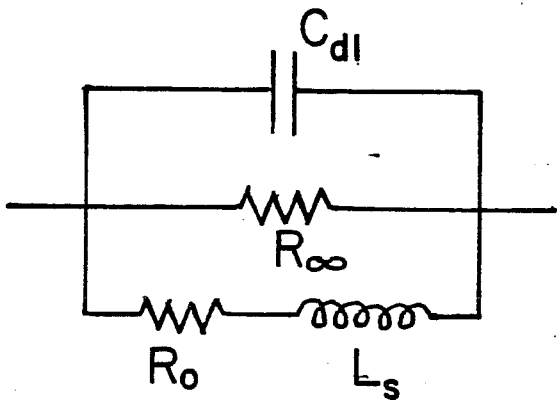
(Ed. Figure 5 to be set as a series/block of 9 graphs arranged as shown on the attached sheet).



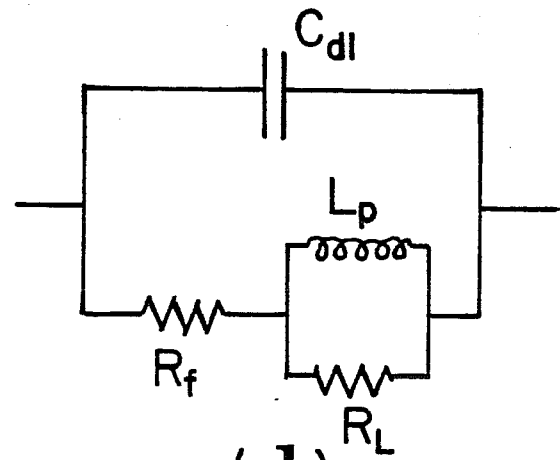
(a)



(c)

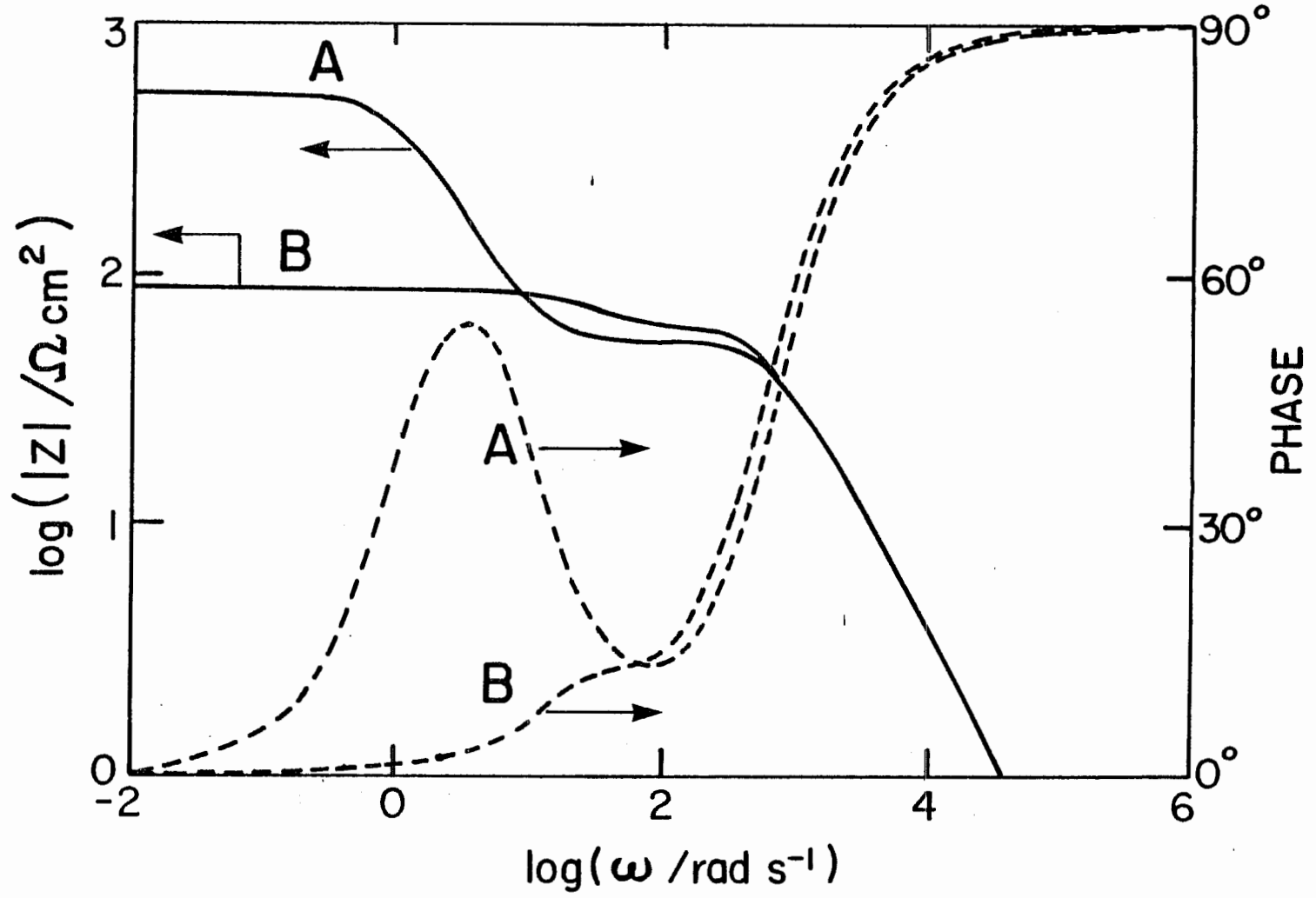


(b)



(d)

Fig 2a



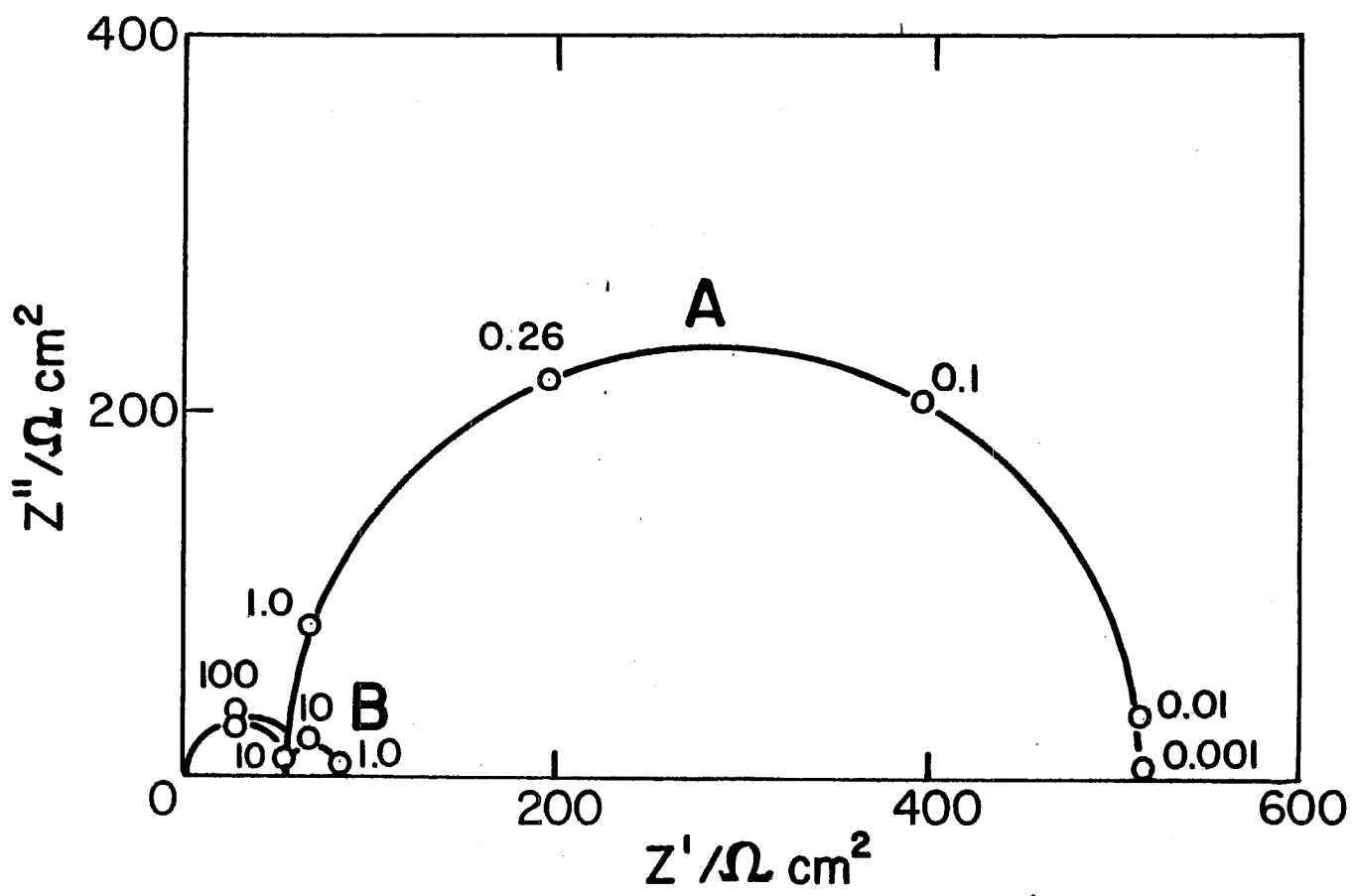
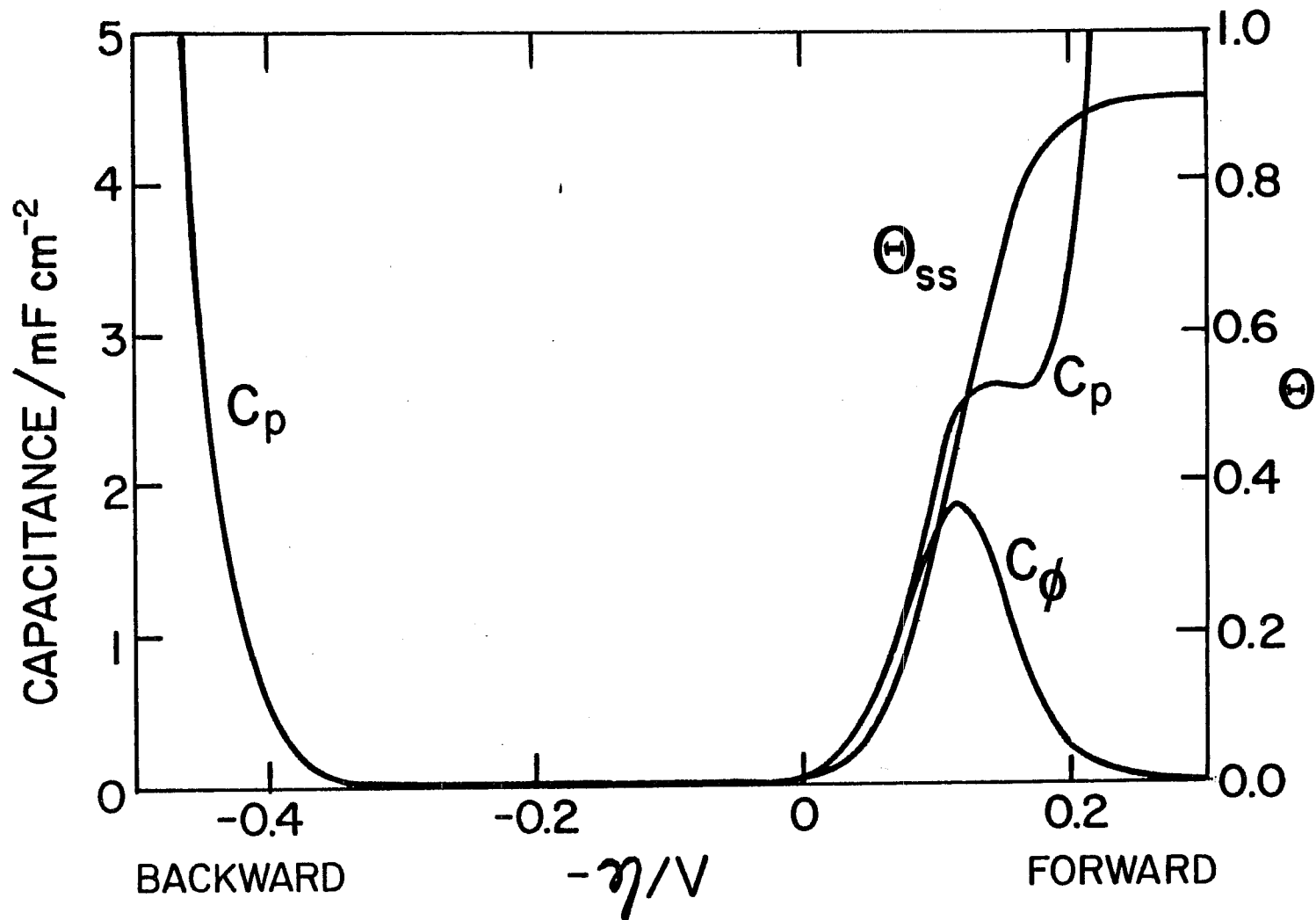


Fig. 3a



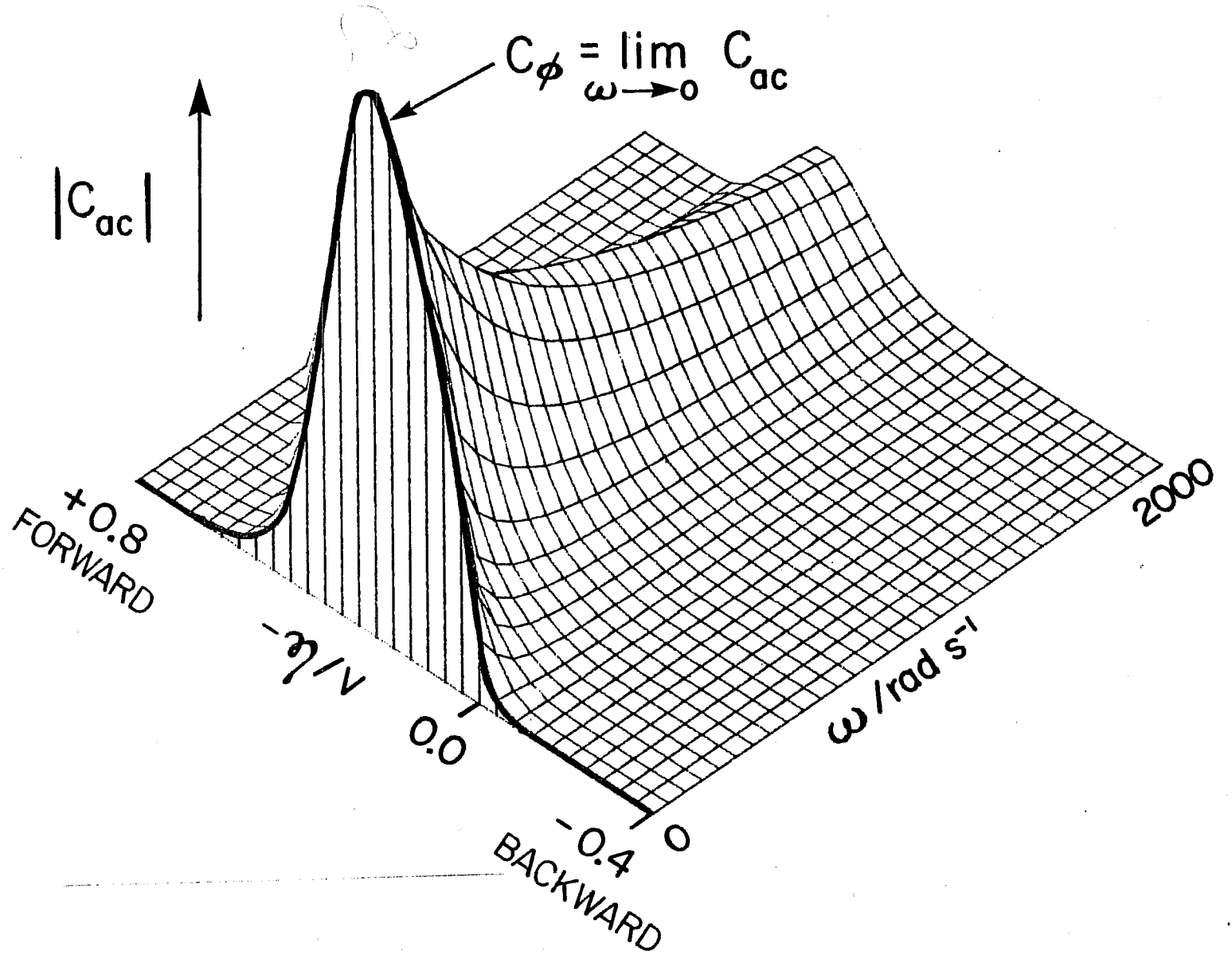
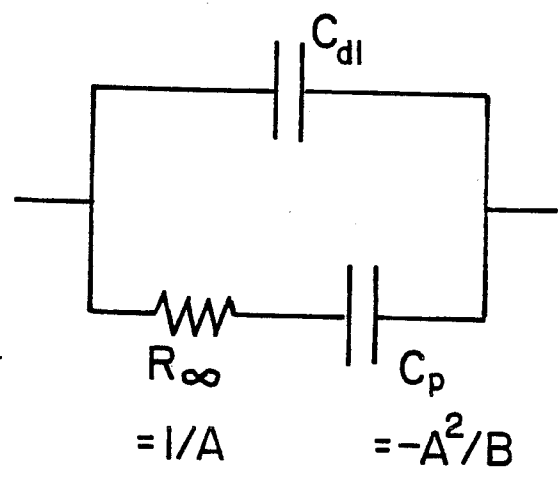
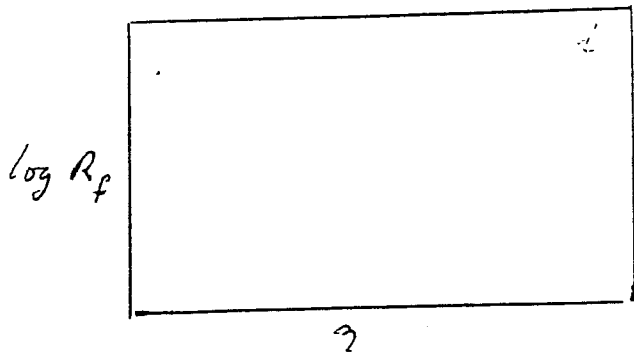
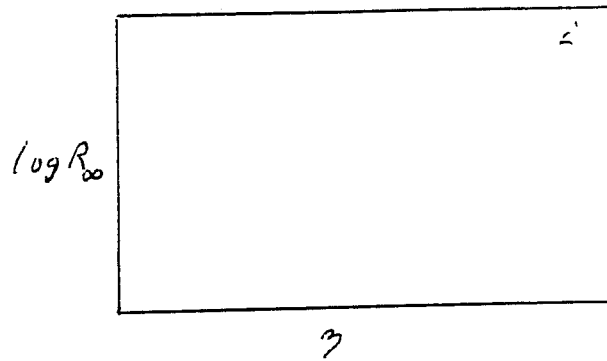
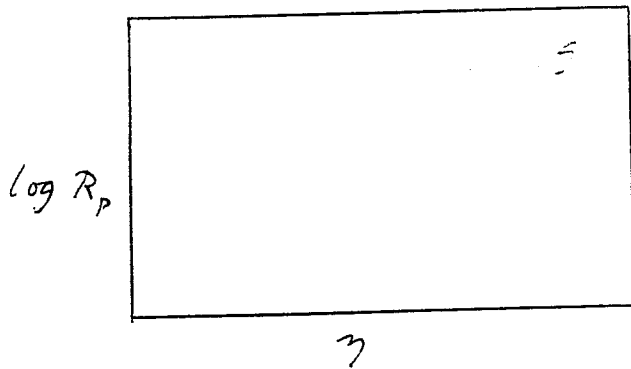
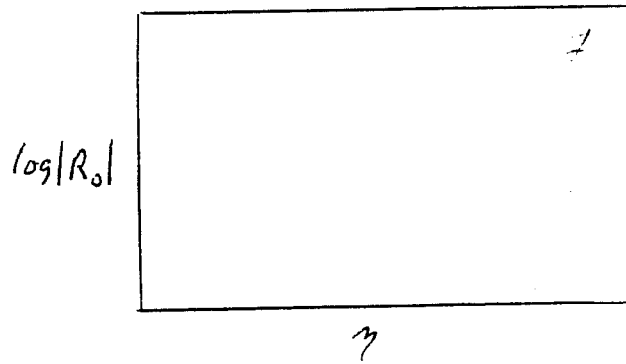
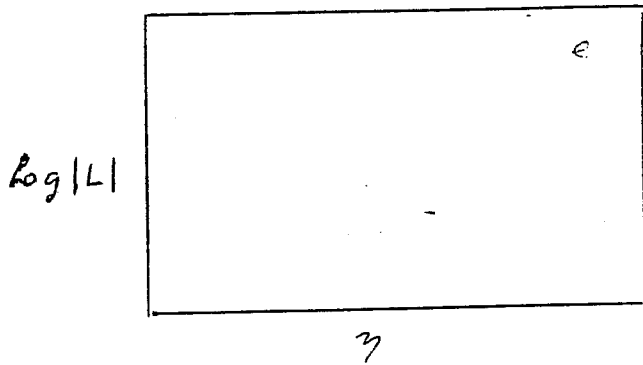
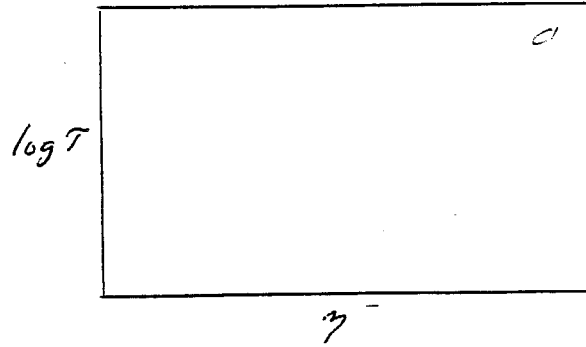
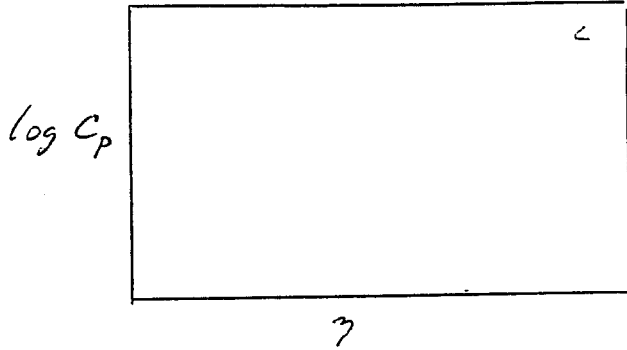
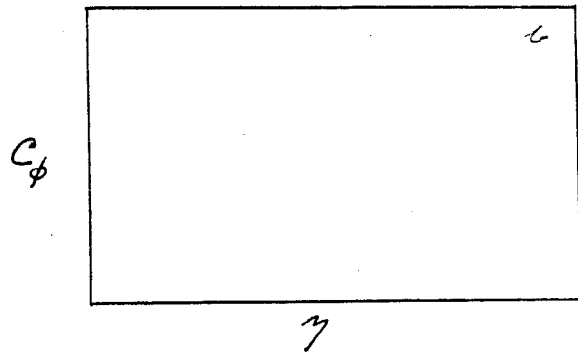
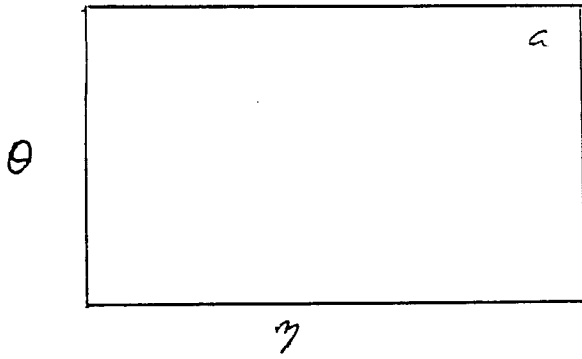
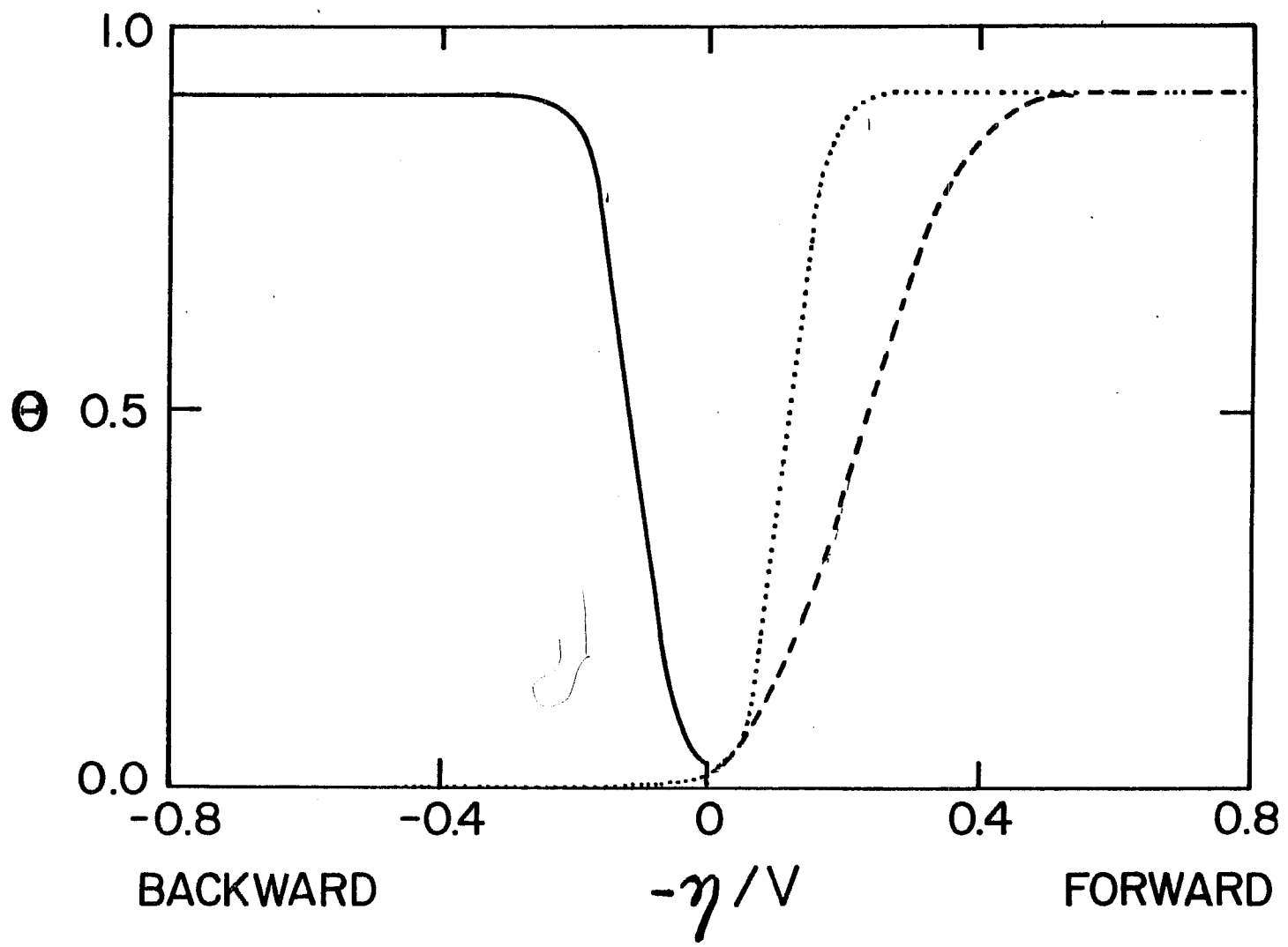


Fig. 4

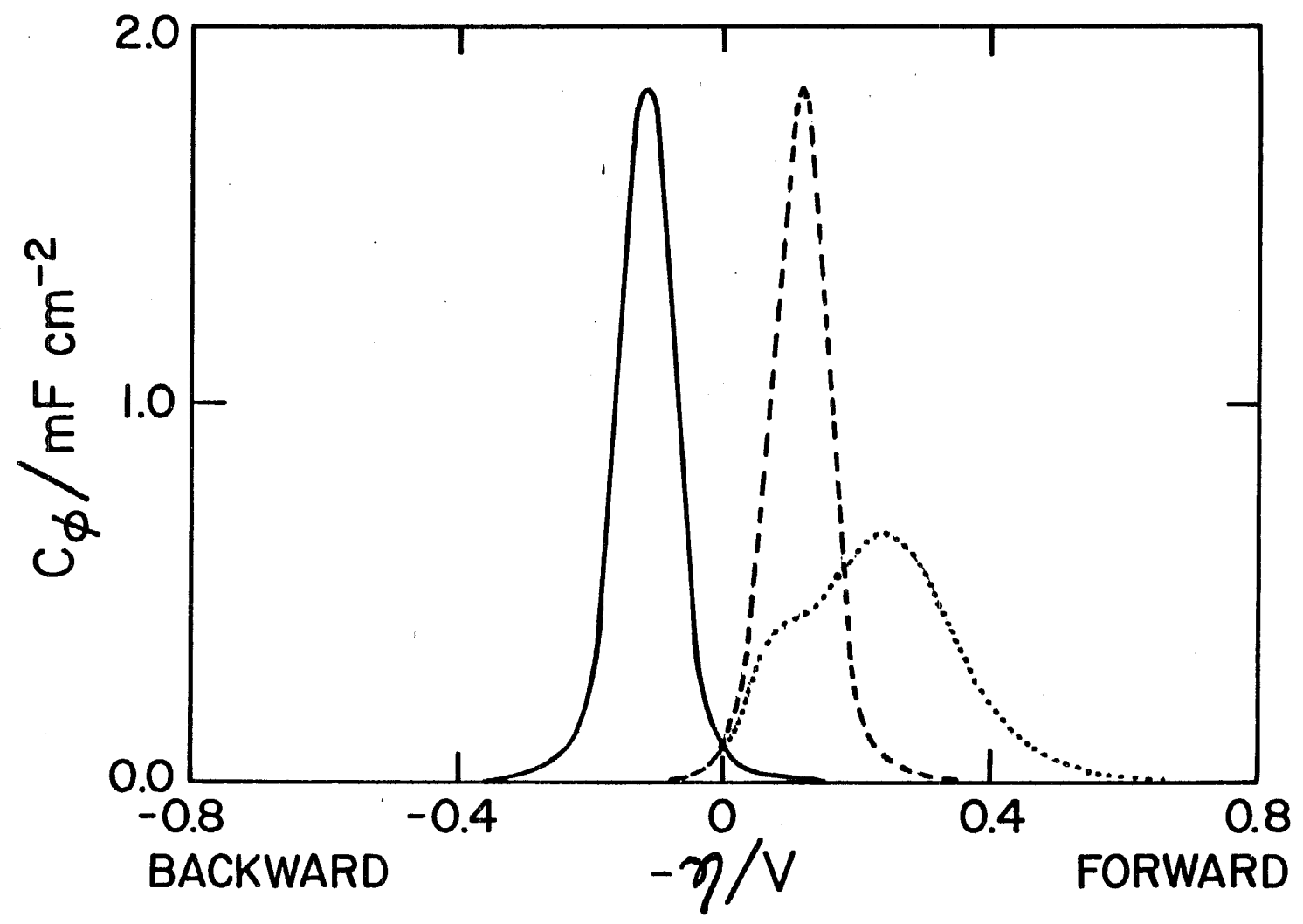


KEY FOR LAYOUT OF FIG. 5

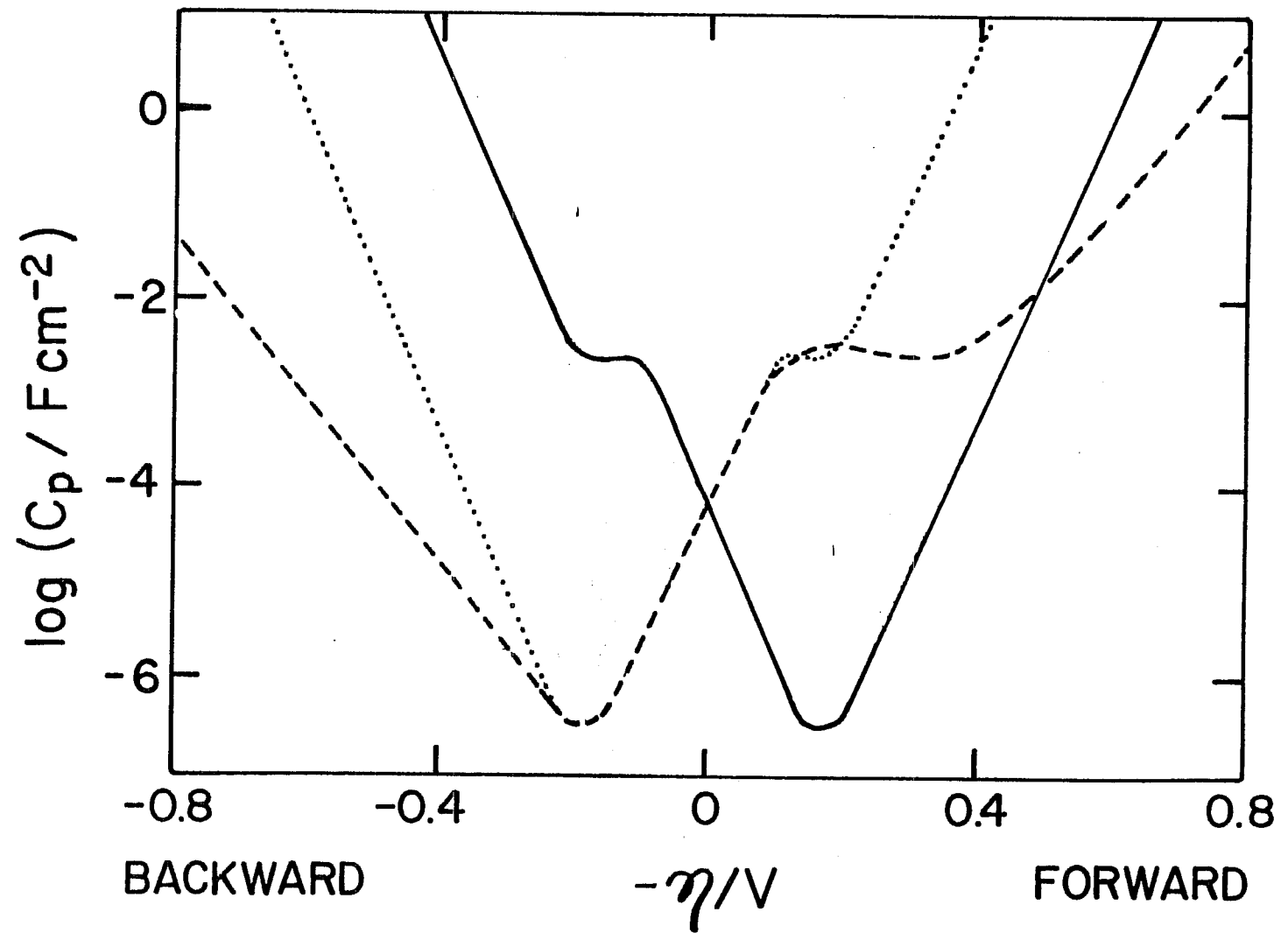




S (d)



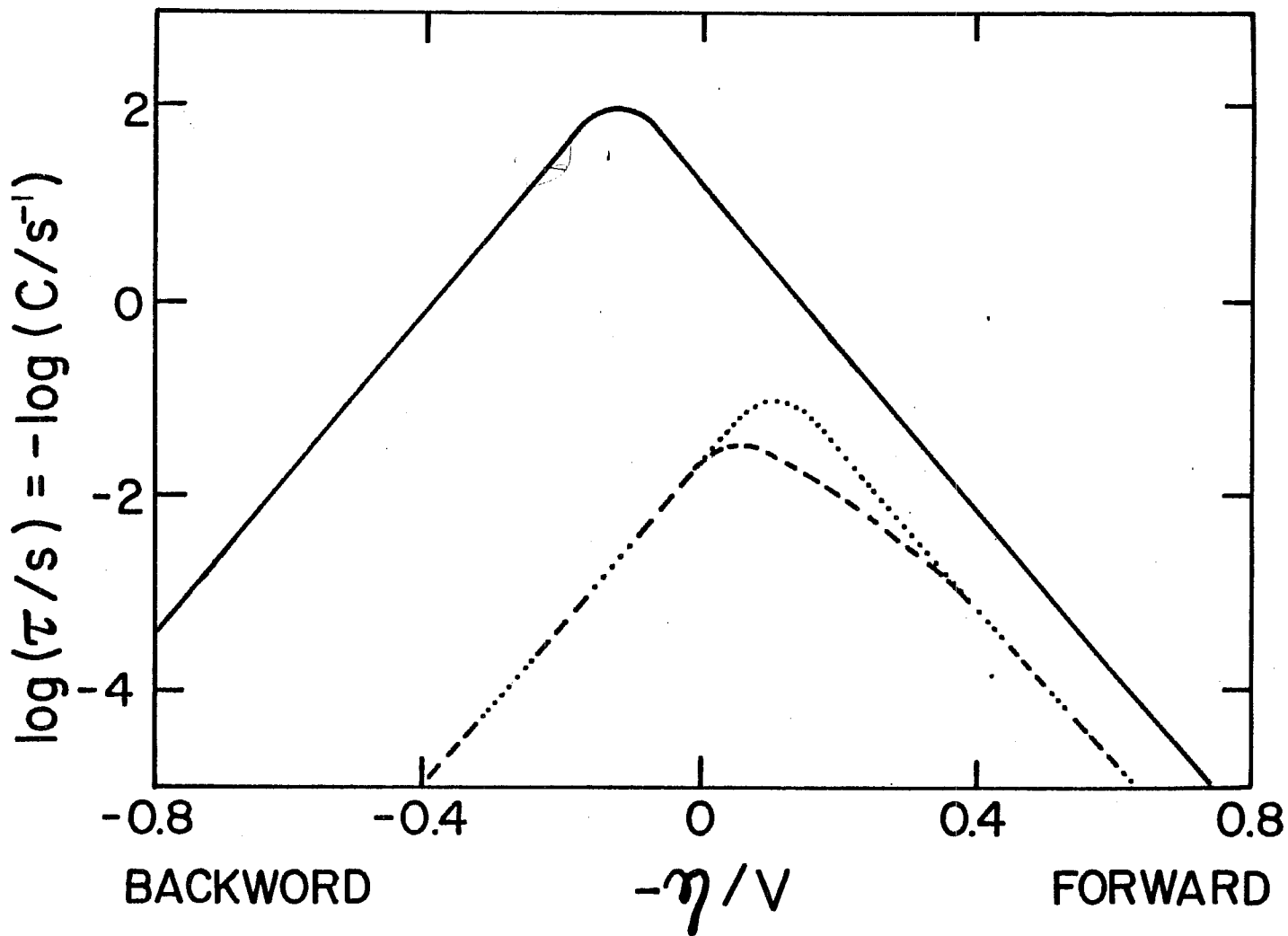
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1.

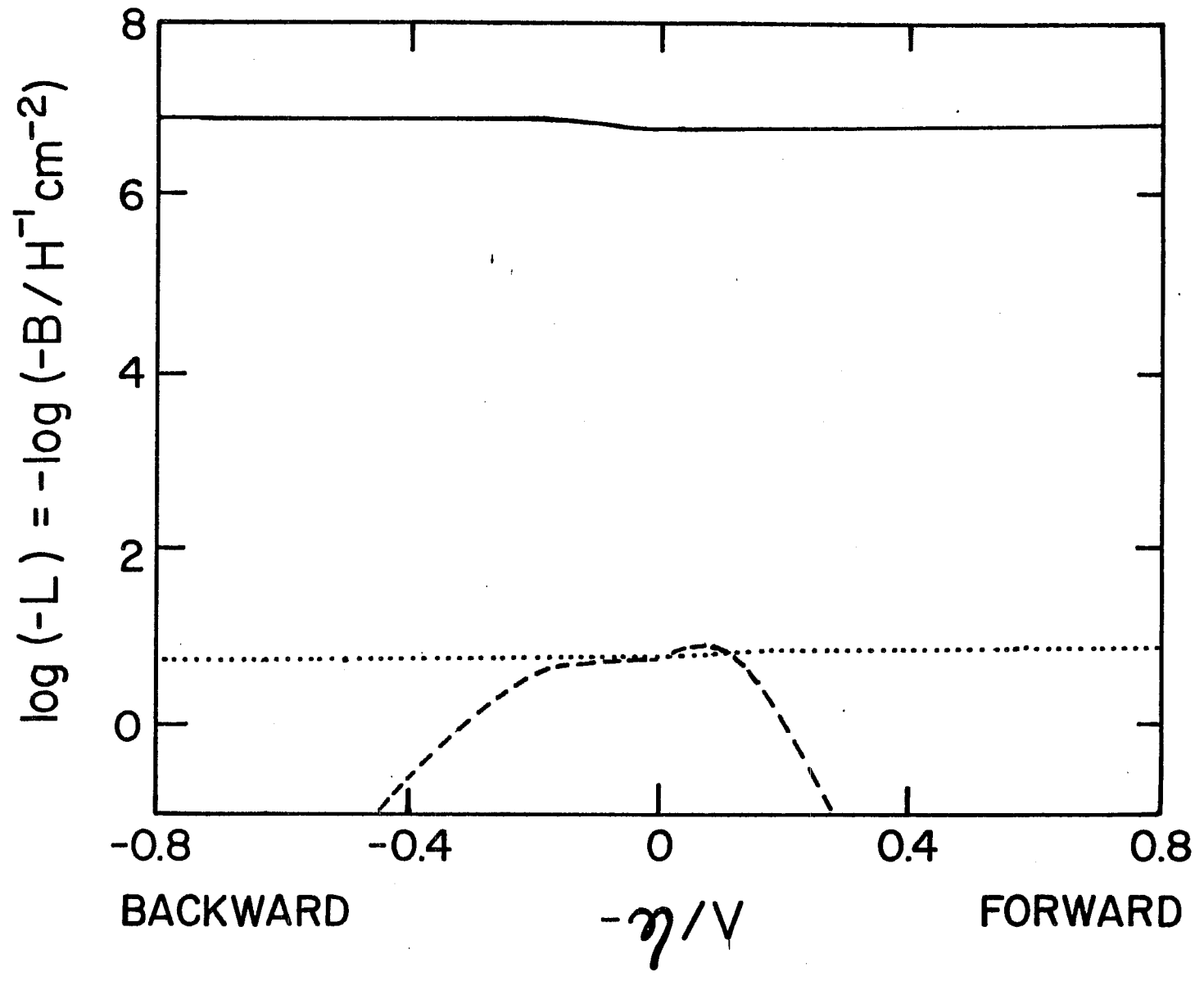
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5(d)



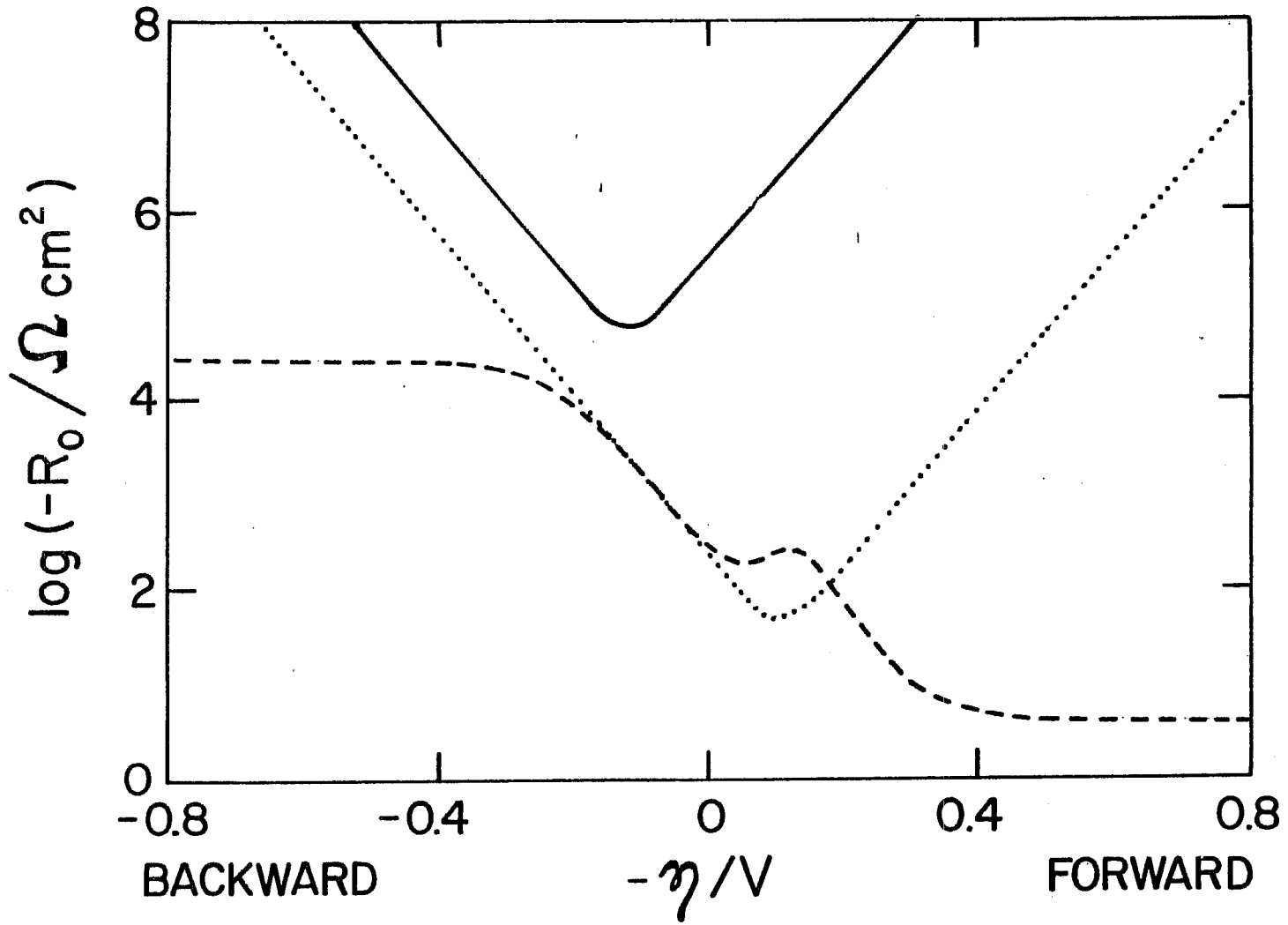
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5(e)

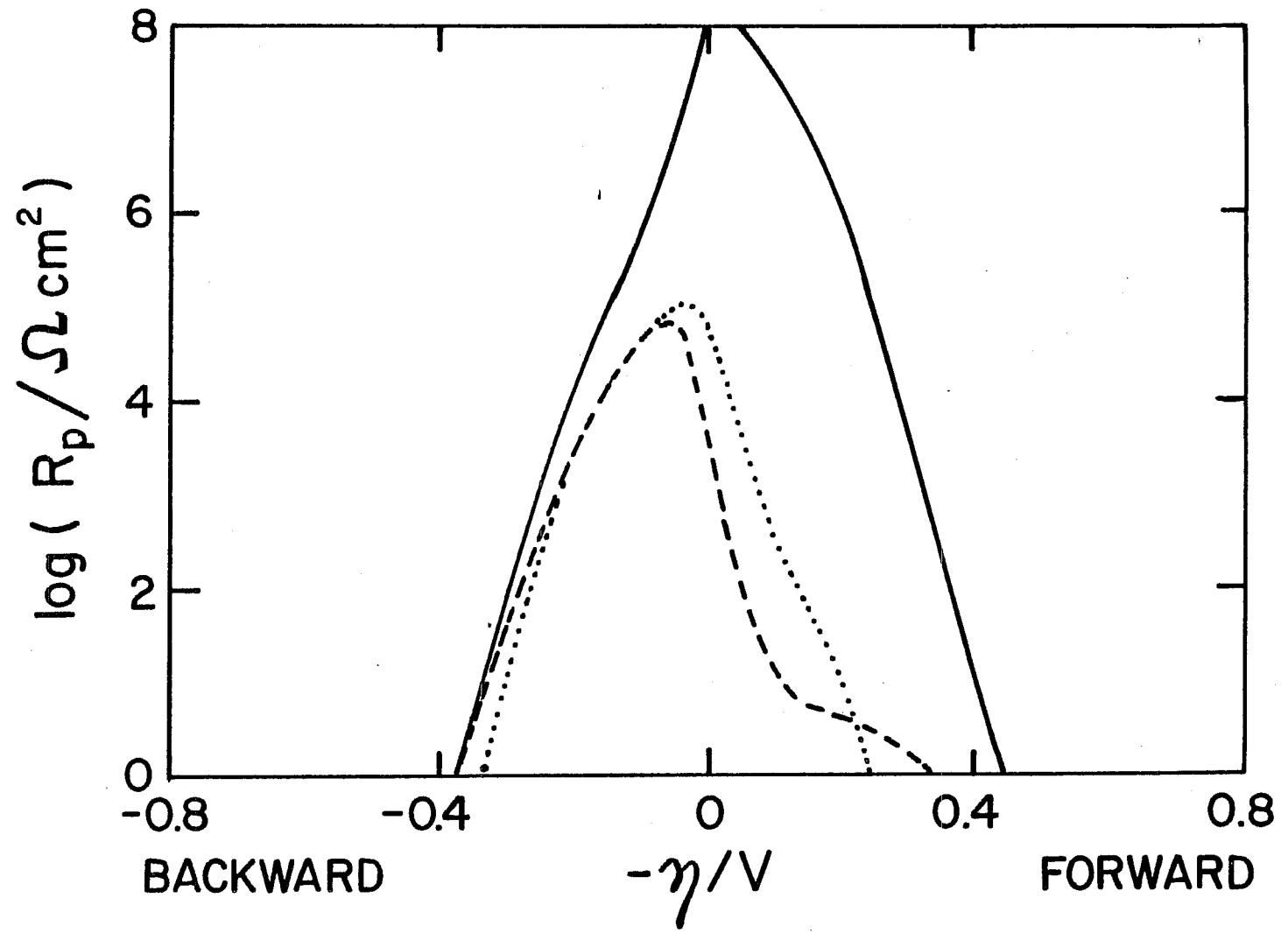


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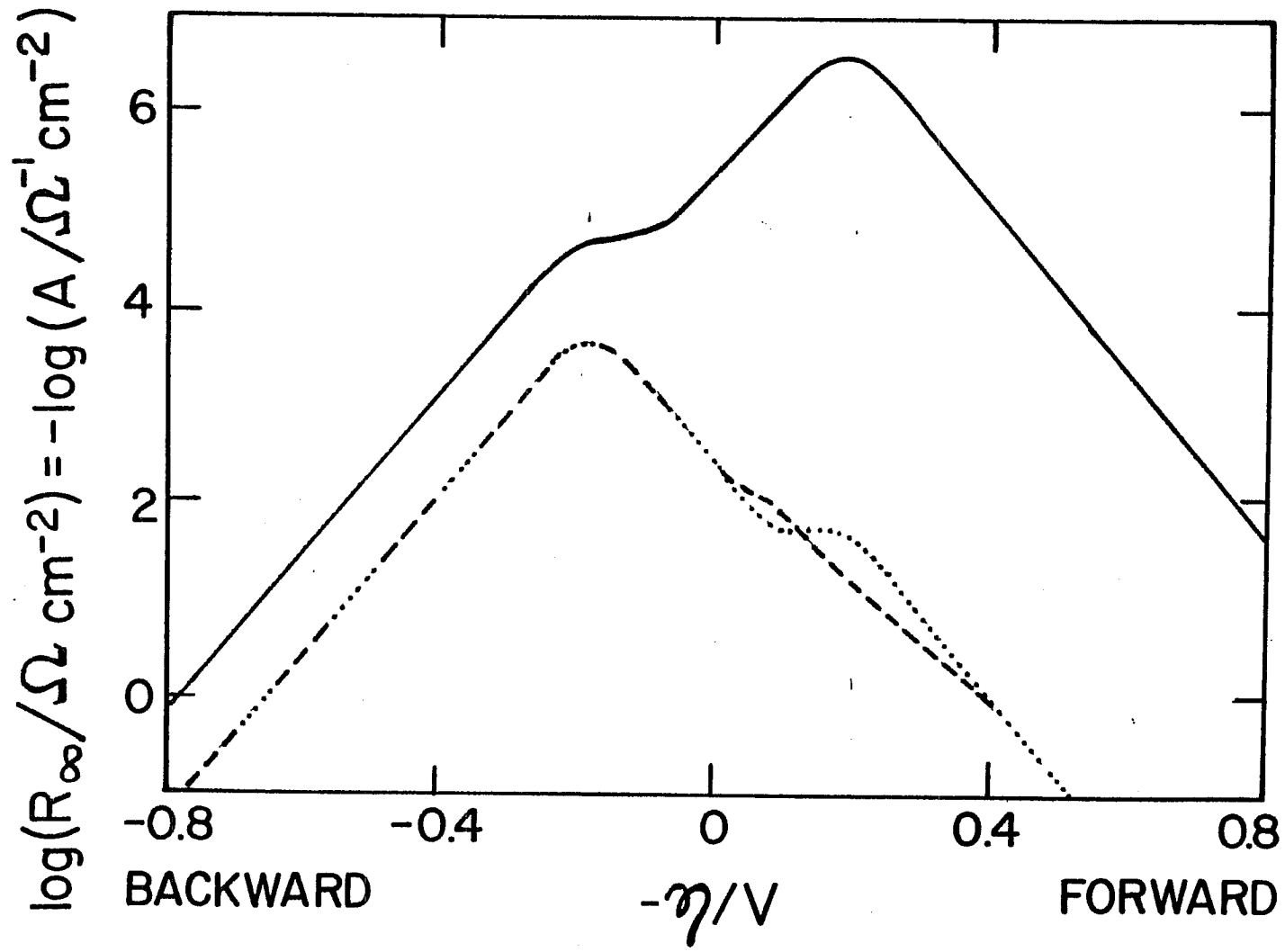
s(f)



f



5 (h)



5