M in the amalgam. The variables are: the potential E, and the concentrations c_+ and c_M just outside the double layers. Thus 12 partial first derivatives are involved in the treatment of small perturbation. Some of these coefficients may be quite negligble, and it may be possible to select experimental conditions that, in effect, lower the number of coefficients to be determined. Furthermore, the three derivatives of i_f can be reduced to a single unknown parameter (exchange current) by the application of the usual current–overvoltage relationship. Only two independent variables are involved for reversible processes and six partial first derivatives are thus required to characterize the double-layer response. It is assumed above that no double-layer kinetic parameter is needed.

(4) The authors state in their conclusion that their method "does not use any *a priori* assumption about the double-layer capacity". Actually some theory is needed, and SLUYTERS and co-workers, to the writer's knowledge, always applied, up to this and the preceding paper[7], the classical impedance theory. They also assumed in their work that the double layer was frequency-independent. These results were most useful and interesting, but SLUYTERS and co-workers used in the explicit formulation of their analysis a theory based on *a priori* separation ideas. It is recognized that the Sluyters analysis allows verification of self-consistency and also the introduction of equations other than those of the classical impedance.

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Received March 8th, 1967

Reply to the comments of P. Delahay[1] on Part XXII of the paper "On the impedance of galvanic cells"

(1). As we reported in our paper[2], our eqn. (9) is identical to eqn. (24) in the paper by DELAHAY AND SUSBIELLES[3]. In our opinion, our derivation is straightforward and is to be preferred to DELAHAY's more intricate derivation. Extrapolation to zero frequency of the concentration fluctuations brought about by periodic perturbations seems an artificial and circuitous way of taking the derivative in the Nernst equation. There could be confusion about the meaning of the symbols $[(C_M)_{x-c}]_{\omega \to 0}$ and $C_M{}^s$ and $C_+{}^s$ in DELAHAY's treatment; this is avoided in our treatment.

(2). Our statement about the significance of the charge separation effect in the absence of specific adsorption is quite intuitively based on the consideration that non-specific adsorption of reactants is negligible if the ionic strength of the supporting electrolyte is sufficiently large compared to that of the reactant (say a ratio of 100:1). From Fig. 2 in ref. 3 it follows that the calculated differential coefficient (ca. 100 μF cm^{-2}) for Zn^{2+} in 0.1 M solution ($i_0 \approx 10^{-2}$), must have a large effect on the cell impedance in the usual frequency range. In a more recent paper[4], the manuscript of which we received after submission of our Part XXII[2], DELAHAY gives a revised version of the quoted figure, from which we infer that the effect is shifted to a lower frequency range, but should still be detectable in normal impedance measurements. To our knowledge, no evidence of departure from classical impedance theory, which might be ascribed to non-specific adsorption of reactants, has so far been published in the literature except for the reference now made by DELAHAY[1] to his own unpublished work. However, he at once makes a reservation, stating that his results are not necessarily explained by non-specific adsorption of Zn^{2+} ions. Although a better equation for mixed electrolytes is used in ref. 4 for calculating the differential coefficients, we are still of the opinion that it is incorrect to insert φ_2-values for the supporting electrolyte alone (without Zn^{2+}) when this leads to such high values of the differential coefficients. For in this case there must exist also a relatively large surface excess of Zn^{2+}, which will increase the φ_2 potential, resulting in a mutual decrease of the differential coefficients. Finally, we note that the basic equation for the more rigorous calculation in the appendix of ref. 4, is taken from the work of JOSHI AND PARSONS[5], who reported an appreciable disagreement between theory and experiment.

(3). We agree with Professor DELAHAY that the frequency range of our measurements may not be sufficiently broad to allow unambiguous assignment of an equivalent circuit. In fact, in Part XXII it is shown only that some equivalent circuits —(a) according to Delahay's equations, (b) according to Reinmuth's equations—may describe the measured impedances in the case of specific adsorption of reactants. On the other hand, our frequency range is sufficiently broad to show that a model of a frequency-dependent capacity *alone*, together with the classical impedance cannot account for the experimental results, because also in the real part of the electrode admittance a considerable attribution of the double-layer impedance is clearly observed.

Extension to lower frequencies would be useful for our analysis method, as this would yield a more reliable value for the Warburg coefficient, σ. With our equipment, measurements on a dropping mercury electrode at frequencies below 220 Hz become difficult, however. With a stationary electrode (*e.g.*, a hanging mercury drop) frequencies down to 20 Hz can be applied. This would be an improvement from the theoretical aspect but accompanied by experimental difficulties in preparing very dilute amalgams (*ca.* 0.5 mM). However, since at lower frequencies the attribution to the cell impedance of the Warburg impedance becomes relatively large, we cannot expect to gain more information on the double-layer impedance from these measurements. Only a more accurate value of σ is obtained; this can be inserted in the impedance equations at higher frequencies in order to evaluate the other parameters.

Extension to higher frequencies is limited by the influence of the ohmic

resistance on the total cell impedance. Reasonably worthwhile measurements are possible up to 8000 Hz, where, in the most favourable case, values for $Z' - R_\Omega$ will be found to be of the order of 1–2 Ω, while R_Ω is of the order of 60 Ω in 1 M solutions. With our equipment, the accuracy in $Z' - R_\Omega$ at 8000 Hz is ca. 0.3 Ω, which is 15–30%. As $Z' - R_\Omega$ is an important quantity needed for the calculation of the cell parameters, we are of the opinion that measurements at frequencies above 2000 Hz may possibly confirm the equivalent circuit adopted for the lower frequencies, but that they are not useful, even for a choice between two circuits, as we attempted in the $Pb^{2+}/Pb(Hg)$ case[6]. In fact, we feel that the new paper by DELAHAY[4] supports our statement that it would hardly be feasible to develop an impedance analysis for the general case of a finite exchange current combined with reactant adsorption (see point 4). We expect more success from a very careful and cautious comparison of the results of a low-frequency and a high-frequency technique (e.g., faradaic rectification).

(4). As regards our earlier work, we feel that some misunderstandings have led Professor DELAHAY to make incorrect statements in some of his publications about "charge separation"[3,4]. Of course some theory is needed, but we have always tried to ascertain which model best describes the experimental results and—to our knowledge—have never created the impression that the assumption of a frequency-independent double-layer capacity is essential in our method. This may be elucidated by formally writing the electrode admittance following DELAHAY[4] as

$$Y'_{el} = 1/R = Y'_f + Y'_{dl} \tag{1}$$

$$Y_{el}'' = \omega C = Y_f'' + Y_{dl}'' \tag{2}$$

where Y_f' and Y_f'' are given by the classical faradaic impedance theory, whereas Y_{dl}' and Y_{dl}'' may be called the components of the double-layer admittance (a posteriori separation). The principle of our method is a careful analysis of Y_{el}' and Y_{el}'' as a function of frequency and d.c. potential[8–10]. There are three distinct possibilities.

(a) There is no significant reactant adsorption, i.e., $Y_{dl}' = 0$ and $Y_{dl}'' = \omega C_d$ if C_d is the double-layer capacitance in the supporting electrolyte. This case manifests itself by the fact that the frequency-dependence of Y_{el}' is found to be in accordance with the classical faradaic impedance theory, yielding consistent values of θ and σ. As an extra check, σ should be related to the d.c. potential by $\sigma = \sigma_m \cosh^2(nF/2\ RT)$ $(E - E_m)$. The value of Y_f'' calculated from θ and σ, can be subtracted from Y_{el}'' to give Y_{dl}'' at different frequencies, so that experimentally it can be verified that $Y_{dl}'' = \omega C_d$.

(b) There is significant reactant adsorption, i.e., $Y_{dl}'' \neq \omega C_d$, but Y_{dl}' is negligible with respect to Y_f'. Again $Y_{el}' \approx Y_f'$ will behave as described under (a), but now Y_{dl}'', calculated in the same way, is not equal to ωC_d. Thus Y_{dl}''/ω (= C_{dl} in DELAHAY's notation) is experimentally determined and may be found to be independent of or dependent on frequency. In this respect our method is different from the modification proposed by DE LEVIE[7], in which the double-layer capacitance is determined by extrapolation to infinite frequency. So far, four examples of this case have been found, namely, $Tl^+/Tl(Hg)$[8], Hg_2^{2+}/Hg[9], $K^+/K(Hg)$[10] and the quinhydrone couple[11]. In all cases, Y_{dl}''/ω appears to be constant in the applied frequency range. It is recognized that the work of DELAHAY has led us to reconsider these results, not for their correctness, but for the interpretation of the observed increase in capacity,

which is to be ascribed to the differential coefficient of the surface excesses of reactants instead of that of the charge density on the electrode surface.

(c) The reactant adsorption is such that Y_{dl}' is a substantial part of Y_{el}'. In this case, the frequency-dependence of Y_{el}' will deviate from "classical behaviour" as we demonstrated for the Pb and In systems[2,6]. In this case *a posteriori* separation of the faradaic admittance is not possible, because its parameters, θ and σ, are not *a priori* known. A rigorous analysis, based on the general equations given by DELAHAY, also seems hardly feasible because of the abundance of differential coefficients and the complexity of the equations.

Finally, we may conclude that our method can be considered as an "*a posteriori* separation" of faradaic and double-layer components, in the sense defined by DELAHAY[3,4]. We gladly recognize that the work of Professor DELAHAY has contributed much to our present views on our own work.

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BOOK REVIEWS

Magnetic Susceptibility by L. N. MULAY, Interscience Publishers Inc., New York, 1966, 123 pages, 23s.

Magnetic susceptibility measurements have a large number of applications in chemistry. Many of these applications and experimental methods will be unknown to the non-specialist in the field. Few chemists are aware, for example, of the fact that particle size determinations on ferromagnetic materials can be made using magnetic susceptibility techniques, and they would probably be little wiser if informed that a coercimeter is used for this purpose. A succinct but up-to-date account of the main experimental methods and of the types of information obtainable by particular techniques, which this book provides, is very welcome. It is in fact a reprint from *Treatise on Analytical Chemistry*, Part 1, Vol. 4, edited by I. M. KOLTHOFF AND P. J. ELVING (Interscience), which appeared in 1963. The pagination has not been