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ON THE DETERMINATION OF THE VALUE OF THE CHARGE OF THE REACTING PARTICLE AND OF THE CONSTANT α FROM THE DEPENDENCE OF THE RATE OF ELECTRO-REDUCTION ON THE POTENTIAL AND CONCENTRATION OF THE SOLUTION*

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Abstract—Consideration of the conditions of electro-reduction reactions at a negatively charged surface leads to the conclusion that the only value that can be unambiguously determined from the dependence of the current strength on the concentration of the supporting electrolyte is the charge of the particles in the bulk of the solution that are in equilibrium with the transition state of the reaction. This conclusion does not depend on concepts about the structure of the double layer and about the location of the reacting particle within the double layer, and is confirmed by the experimental data on the reduction of $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$ and H_3O^+ ions. On the contrary, the value of the constant α obtained from the experimental data strongly depends on these assumptions and, consequently, the determination of α in the case of pronounced ψ_1-effects gives only very approximate values. Some conclusions about the location of the centre of the particle in the transition state of the reaction can be made by comparsion of polarization curves obtained with mercury and with thallium-amalgam electrodes.

Résumé—L'analyse des conditions d'électroréduction cathodique montre que la seule grandeur déterminable sans ambiguïté, d'après la relation entre le courant et la concentration de l'électrolyte support, est la charge des particules du sein de la solution en équilibre avec l'état de transition. Cette conclusion n'implique aucune hypothèse sur la structure de la couche double, ni sur la localisation dans cette couche de la particule réagissante. Elle est confirmée par les résultats expérimentaux obtenus en réduisant les ions $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, H_3O^+. Au contraire, le calcul de la constante α au moyen de ces résultats implique de telles hypothèses et ne saurait donc être que grossièrement approché s'il y a des effets ψ_1 prononcés. Des indications sur la localisation du centre de la particule dans l'état de transition peuvent néanmoins être fournies par comparaison des courbes de polarisation respectivement obtenues avec électrodes de mercure et d'amalgame de thallium.

Zusammenfassung—Die Analyse der Bedingungen, unter denen der Reduktionsvorgang an einer negativ-geladenen Elektrodenoberfläche verläuft, führt zu dem Schluss, dass die einzige Grösse, welche eindeutig auf Grund der Abhängigkeit der Reaktionsgeschwindigkeit von der Konzentration des indifferenten Elektrolyten ermittelt werden kann, die Ladung der gelösten Teilchen ist, welche sich im Gleichgewichte mit dem Übergangszustande der Reaktion befinden. Dieser Schluss hängt nicht von unseren Voraussetzungen über den Bau der Doppelschicht und über die Lage des Teilchens im Übergangszustande der Reaktion innerhalb der Doppelschicht ab. Er wird durch experimentelle Resultate bestätigt, die mit $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$ und H_3O^+ erhalten wurden. Demgegenüber hängt die aus experimentellen Daten ermittelte Grösse der Konstante α wesentlich von diesen Voraussetzungen ab, weshalb die Bestimmung von α im Falle ausgesprochener ψ-Effekte nur näherungsweise durchgeführt werden kan. Einige Schlüsse bezüglich der Lage des Ladungszentrums im Übergangszustande der Reaktion kann man aus der Zusammenstellung der Polarisationskurven ziehen, welche mit Quecksilber und Thalliumamalgamelektroden erhalten wurden.

AT PRESENT there is considerable experimental evidence available which proves the effect of the electric double layer structure on the kinetics of the electrode processes. These effects are most pronounced in the cases when the reacting particle carries a high charge. The quantitative interpretation of the results obtained, however,

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in a number of cases led to contradictory conclusions[1,2]. In the present communication we shall try to ascertain to what extent the measurements of the dependence of the current strength on the potential and the concentration of the supporting electrolyte under the conditions of a steady electrolysis permit us to draw conclusions about the nature of the reacting particle and about the value of the Tafel constant α in the case of an irreversible electrochemical process of the first order.

Let us consider first the problem of the determination of the charge of the reacting particle. If we assume that with a constant concentration of the reacting particles in the surface layer, the kinetics of the electrochemical process obeys Tafel's equation, and that there exists an equilibrium between the transition state of the reaction and the reacting particles in the bulk of the solution, then by taking into account the effect of the electric field of the double layer, we obtain for the rate constant k of a one-electron reduction process[1]

$$k = k_0 \exp \frac{F}{RT}[-\alpha(\varphi - \psi_1) - n_1\psi_1], \tag{1}$$

where n_1 is the charge of the reacting particle in the bulk of the solution, ψ_1 the potential at the point where the centre of the charge of the transition state of the reaction is located, due to the remaining charged particles, φ the metal/electrolyte potential difference, $0 < \alpha < 1$. From the departures from equation (1) observed conclusions were drawn about the different charge of the reacting particle in the surface layer and in the bulk of the solution (formation of ionic pairs), and also about other forms of interaction of the reacting anion with the cations of the double layer.[2]

To verify equation (1) it is necessary to know the dependence of ψ_1 on φ and on the concentration of the supporting electrolyte, which necessitated certain assumptions to be made about the structure of the double layer and about the position of the reacting particle relative to the ions of the supporting electrolyte in the double layer. A very simple assumption would be to equate ψ_1 with the mean value of the potential in the outer Helmholtz layer (Grahame's ψ_0), but there is no certainty about its correctness. Moreover, there are a number of approximations in the calculation of ψ_0, e.g. no allowance being made for the discrete structure of the double layer, for the surface coverage, etc.

Let us show that these difficulties can be avoided in the case of a surface carrying a sufficiently high negative charge. For this purpose, let us confront the course of the reactions of electron transfer to the particle M^{n_1} in two systems I and II with identical values of $C_r = [M^{n_1}]$, satisfying the following conditions.

(1) The surface densities of the anions of the supporting electrolyte Γ_A and of the reacting anions are small compared to that of the cation Γ_K, i.e. $|\Gamma_A| \ll |\Gamma_K|$. In the case of dilute solutions and not too low values of the charge density ε it follows from this inequality that at sufficiently small distances from the interface the concentration of anions compared to that of cations can be neglected.

(2) During the transition from system I to system II, the following relation is fulfilled:

$$\varphi - \left(\frac{RT}{n_2F}\right) \ln c = \text{const},$$

where n_2 is the charge, c the concentration of the cations of the supporting electrolyte (the solution being assumed to contain only cations with identical charge values).

In the case of dilute solutions, it follows from the basic thermodynamic equation of electrocapillarity* that

$$d\sigma = -\varepsilon\, d\varphi - RT\Gamma_A\, d\ln c - RT\Gamma_K\, d\ln c \tag{2}$$

(σ is the metal/solution interfacial tension). By taking into account condition (1) and that of electroneutrality, which in our case amounts to $\varepsilon = -n_2\Gamma_K F$, we obtain

$$\left(\frac{\partial\varepsilon}{\partial \ln c}\right)_\varphi = -\frac{RT}{n_2 F}\left(\frac{\partial\varepsilon}{\partial\varphi}\right)_{\ln c} \tag{3}$$

$$\varepsilon = f\left(\varphi - \frac{RT}{n_2 F}\ln c\right), \tag{4}$$

which combined with condition (2), leads to $\varepsilon = \text{const}$. To the invariance of ε corresponds the invariance of the dependence of the potential on the distance at small enough distances from the surface, at which condition (1) is fulfilled.

In fact, by assuming provisionally the potential in the metal in the two systems to be equal to 0 and by writing down the expressions for the electrochemical potentials of the cations $\mu_K = \mu_K{}^0 - \varphi n_2 F + RT\ln c$ at an infinite distance from the interface, we arrive at the conclusion about the equality of μ_K when condition (2) is observed. Since, in accordance with condition (1), only cations participate in the equilibrium in the vicinity of the interface, we can infer from the equality of μ_K that the surface layer has an identical composition and structure in systems I and II†. Hence follows the invariance of $\varphi - \psi_x$ upon the transition from system I to II and, consequently, the relation

$$\psi_x = \text{const} + \frac{RT}{n_2 F}\ln c, \tag{5}$$

where ψ_x is the potential at the distance x from the interface (here and henceforth the potential is referred to a point in the bulk of the solution).

Thus, by studying the kinetics of processes in the systems for which condition (2) is fulfilled, it is possible to establish the effect upon the rate of the process of the difference of potentials between the point at which the reacting particle is located in the surface layer and the bulk of the solution, with the other conditions controlling the reaction course being identical. At constant bulk concentration of the reacting particle, its concentration in the vicinity of the electrode surface (at distances at which condition (1) is fulfilled) changes in proportion to $\exp(-n_1\psi_x F/RT)$. Hence, the rate of the process is proportional to c^{-n_1/n_2} or

$$\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\varphi-(RT/n_2F)\ln c,\ Cr} = -\frac{n_1}{n_2}. \tag{6}$$

This conclusion does not depend on the assumptions on which the theory of the diffuse double layer is based and remains valid at any surface coverage, as well as in the case of a specific adsorption of the ions of the supporting electrolyte and of the reacting

* For non-ideal solution, activities $a_\pm$ must be substituted for concentrations.

† This conclusion requires a certain limitation, namely, anions are present in the solution beyond the layer in which their concentration can be neglected. Since the coulombic forces are far-reaching, the presence of these anions may affect the structure of the double layer also at intermediate distances where their concentration is still small.

particle, so long as condition (1) is fulfilled*. The result is also independent of the character of interaction of the reacting particle with the cations of the double layer, in particular, of the formation of ionic pairs in the double layer.

The dependence of the kinetics of the process on c is thus determined by the charge of the particles in the bulk of the solution and cannot be used as a diagnostic criterion in the establishment of the effective charge of the reacting particle in the double layer, although the rate of the reaction at a definite c depends on it. The same result was arrived at earlier in considering the equilibrium between the ionic pairs in the bulk of the solution and at the surface.[4]

A comparison of the kinetics in the systems for which the condition $\varphi - (RT/n_2F) \ln c = \text{const.}$ is fulfilled was used for the first time in a rigorous deduction of the independence of the hydrogen overvoltage of the concentration in acid solutions, containing no supporting electrolyte[5].

Gierst[2] used the following equation which he deduced from equation (1), in the determination of the value of n_1:

$$\left(\frac{\partial \ln i}{\partial \psi_0}\right)_{\varphi-\psi_0} = -\frac{Fn_1}{RT}, \tag{7}$$

It becomes identical to equation (6), if the approximate relation known from Gouy's theory of the double layer,

$$\psi_0 = \text{const} + \frac{RT}{n_2F} \ln c, \tag{8}$$

is taken into account.

Gierst assumed, however, the value n_1, found from equation (7), to express the effective charge of the reacting particle in the double layer, whereas, as follows from the above, n_1 represents the charge of the particle in the bulk of the solution, which is in equilibrium with the transition state of the reaction, the bulk concentration of the reacting particle remaining constant with a change in c.

Since the anion concentration can be neglected in comparison with the concentration of cations only at not too large distances from the interface, it is possible by the verification of equation (6) to ascertain approximately the upper limit of the distance at which the reaction occurs. For this purpose, however, it is necessary already to make definite assumptions concerning the structure of the diffuse double layer. It follows from Fig. 1 calculated on the basis of Gouy's theory of the diffuse double layer that the departure from the invariance of the value $\psi_x - (RT/n_2F) \ln c$ in the case of transition from 10^{-3} N to 10^{-2} N solution occurs at distances from the outer Helmholtz plane exceeding 15 Å and, in the case of a transition from 10^{-2} N to 10^{-1} N solution, at distances >5 Å.

It should be noted that in the case when the equilibrium between the transition state of the reaction and the reacting particles in the solution is not observed

* Instead of the equilibrium between the reacting particle in the bulk of the solution and that in the surface layer, the equilibrium with the particle in the transition state of the reaction may be considered, which gives the same results, as was shown for the case of the H_3O^+-ion discharge.[3] In fact, if the transition state is considered as that in which a fraction α of a positive charge is neutralized by an electron, the probability of the transition state is proportional to

$$\exp\left[-\frac{n_1\psi_x F}{RT} - \frac{\alpha(\varphi - \psi_x)F}{RT}\right],$$

which leads to the same result, since $\varphi - \psi_x = \text{const}$.

("dynamic" ψ effect), the analysis of the dependence of ln i on ln c also leads to the charge of the particles in the bulk of the solution.*

The possibility of a rigorous determination of the value n_1 depends only on the strict observation of condition (1) and, consequently, of equation (4). The latter can be checked, independently of kinetic measurements, by means of the ε, φ curves, or by the shift of the descending branch of the electrocapillary curves in the function of c. It follows from Frumkin's measurements,[7] as well as from the ε, φ curves calculated by means of differential capacity values determined in LiCl, NaF, KCl and CsCl

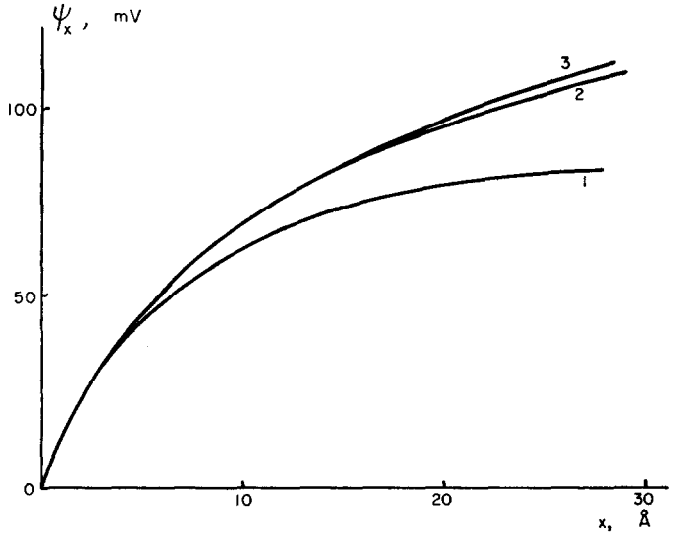

FIG. 1. Distribution of potential in the diffuse layer referred to the potential at the outer Helmholtz plane for solutions of a 1–1 valent electrolyte in concentrations: (1) 10^{-1} N; (2) 10^{-2} N; (3) 10^{-3} N; at $\varepsilon = -10\,\mu C/cm^2$.

solutions of various concentrations,[8,9] that equation (4) is observed in the case of the solutions studied within the accuracy of measurements. An increase of the accuracy of this verification is desirable.

The method of calculation just considered can be also used in the case when the anion reduced R^{n_1}, is obtained as the result of a reaction preceding the electrochemical step $A^n \rightleftarrows R^{n_1} \pm pX^m$ ($n = n_1 \pm pm$). If the process rate is determined by the slow discharge of R^{n_1} under the conditions of an equilibrium between the bulk of the solution and the surface layer, and the supporting electrolyte does not influence the ratio $[A^n]:[R^{n_1}]$, an analysis of the ln i vs. ln c dependence will lead to the charge of R^{n_1}. If the electrolyte added contains anions capable of affecting the chemical equilibrium, it is necessary to take into account the departure from the condition of the constancy of the bulk concentration of R^{n_1}. When A^n and R^{n_1} are reduced simultaneously, the shape of the curve plotted in the coordinates ln i — ln c must depend on the change in the ratio $[A^n]:[R^{n_1}]$, if the electrolyte added contains X^m. The role played by the

* In fact, according to Levich's theory,[6] the rate constant of anion reduction with a supporting 1–1 valent electrolyte is proportional to $\Lambda^{-1} \exp\,(|n_1| - \frac{1}{2})(F\psi_1/RT)$, where Λ is the Debye length. By using (5) and taking into account the proportionality of Λ to $c^{-1/2}$ we obtain

$$\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\varphi-(RT/n_2F)\ln c} = -\frac{n_1}{n_2}$$

anion with the higher charge in the electrochemical process must diminish with a decrease in c and an increase in $-\varphi$, in accordance with the corresponding rise of $-\psi_1$. If the process rate is determined by the slow establishment of the equilibrium of the reaction considered and the thickness of the reaction layer is small compared to that of the double layer, by taking into account the Boltzmann distribution for A^n and X^m, which are in equilibrium with the bulk of the solution, we arrive at the conclusion that the method suggested will again lead to the charge of R^{n_1}. Thus, although the consideration of the dependence of ln i on ln c permits us to draw a conclusion about

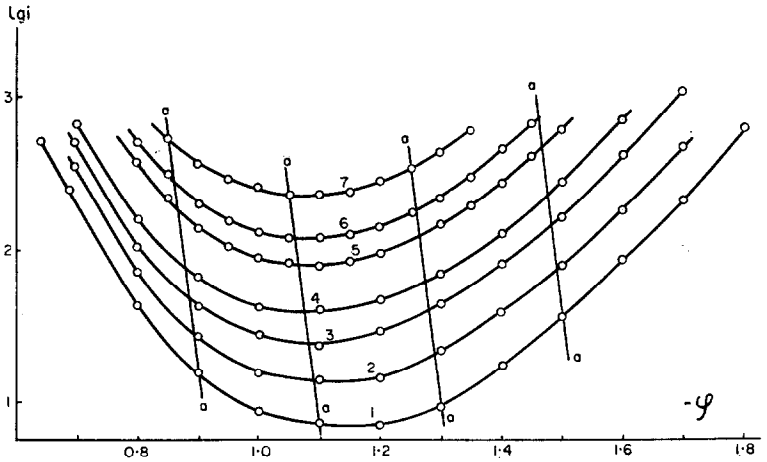

FIG. 2. Dependence of the reduction rate of 10^{-3} N $Na_2S_2O_8$ on the potential in the presence of NaF in concentrations: (1) 3×10^{-3} N; (2) 5×10^{-3} N; (3) 7×10^{-3} N; (4) 10^{-2} N; (5) $1{\cdot}5 \times 10^{-2}$ N; (6) 2×10^{-2} N; (7) 3×10^{-2} N; (here and below φ in V referred to N.C.E., i in $\mu A/cm^2$).

the value of n_1, it does not provide an answer to the question whether the process rate is determined by a chemical reaction in the double layer preceding the electrochemical step, or by the slow electrochemical step itself.

The verification of relation (6) for the reduction of H_3O^+ on mercury by means of experimental data[10,11] results in the values of n_1 which lie in the limits 0·9–1.

We determined the i,φ curves of the reduction of 10^{-3} N $Na_2S_2O_8$, $K_2S_2O_8$ and $Cs_2S_2O_8$ with the help of a dropping mercury electrode with supporting electrolytes of various concentrations: NaF and NaCl from 3×10^{-3} N to 3×10^{-2} N, KCl from 2×10^{-3} N to 10^{-2} N and CsCl from 5×10^{-4} to 5×10^{-3} N, as well as the i,φ curves of 10^{-3} N $Na_2S_2O_8$ solutions in the presence of various concentrations of LiCl + NaCl (from 10^{-2} N to 7×10^{-2} N), the ratio $[Li^+]:[Na^+]$ being held constant and equal to 10. The curves measured in the solutions containing NaF and NaCl respectively practically coincided at potentials more negative than the point of zero charge. After making an allowance for the concentration polarization according to the theory of Meiman and Bagotsky (Frumkin *et al.*[4]), the quantity n_1 was calculated as shown in Fig. 2 (the aa lines connect the points corresponding to the condition $\varphi - (RT/n_2F) \ln a^+ = \text{const}$). The values of $-n_1$ calculated for various ε lie within the limits 1·73–1·86 with LiCl + NaCl as supporting electrolyte, 1·75–1·92 with NaF, 1·87–1·96 with KCl and 1·90–1·96 with CsCl, being the closer to $-n_1 = 2$, the larger is $-\varepsilon$.

In the case of reduction of $S_2O_8^{2-}$ with a NaF supporting electrolyte, our experimental data are at variance with those of Gierst[2], which he himself considers, however, to be only preliminary. The conclusion drawn by Gierst about the difference in the charge of the reacting particle during the reduction of $S_2O_8^{2-}$ at potentials of the descending and ascending branches of the curve are not confirmed by our data.* Apparently, the somewhat lower values of $-n_1$ obtained with LiCl as supporting electrolyte can be explained by higher concentrations of the supporting electrolyte which had to be used in that case in view of a lower process rate, which resulted in an inferior fulfillment of condition (1). In general, incomplete observance of condition (1) probably accounts for lower values of $-n_1$ than expected from the theory. The calculation of n_1 for the reduction of $Fe(CN)_6^{3-}$ by means of the data of Ref. 4 gives the values $-2{\cdot}7$ for LiCl as supporting electrolyte and $-3{\cdot}0$ for KCl and CsCl.

In the case of reduction of $PtCl_4^{2-}$ with KCl as supporting electrolyte, the $\ln i$ vs. $\ln a_{\pm}$ dependence is expressed by a curve with a slope in its initial part smaller than 1 and increasing to 2 with [KCl] $> 0{\cdot}1$ N. With CsCl as supporting electrolyte, the slope of the $\ln i$ vs. $\ln a_{\pm}$ straight lines is between 1 and 2. These results can be explained if we assume that in $PtCl_4^{2-}$ solutions there are also present, due to the hydrolysis of the complex, $PtCl_3H_2O^-$ anions and perhaps uncharged particles of $PtCl_2(H_2O)_2^0$ as well, which are also reduced, and if we take into account the change in the concentration of the particles with an increase in Cl^-. The presence of these entities in $PtCl_4^{2-}$ solutions has been established by various methods and confirmed by the calculations on the basis of equilibrium constants and rate constants of the hydrolysis reactions.[12]

In contrast to the determination of the charge, the calculation on the basis of experimental data of the transfer coefficient α in the presence of pronounced ψ_1-effects, can be only an approximate one, since it necessitates the knowledge of the dependence of ψ_1 on φ and on the concentration of the supporting electrolyte, and, consequently, depends on the assumptions concerning the double layer structure and the location of the centre of the particle in the transition state of the reaction within the double layer.

For the determination of α it is convenient to use relation (9), resulting from equation (1):

$$\lg i + \frac{n_1\psi_1 F}{2{\cdot}3RT} = \text{const} - \frac{\alpha F}{2{\cdot}3RT}(\varphi - \psi_1), \tag{9}$$

and to plot the experimental data in the coordinates $[\lg i + (n_1\psi_1 F/2{\cdot}3RT)]$, $(\varphi - \psi_1)$. This method was used by Asada *et al.*[13] The straight lines with a slope of $\alpha F/2{\cdot}3RT$ in these co-ordinates were termed corrected Tafel plots.

Let us suppose initially that the centre of the charge in the transition state is localized in the outer Helmholtz plane and $\psi_1 = \psi_0$. The value of the transfer coefficient obtained under these assumptions will be designated by α_0.

To calculate the ψ_1-potentials we used the ε,φ curves determined in 10^{-1} and 10^{-2} N NaF[14] and in 1 N, 10^{-1} N and 10^{-2} N LiCl, KCl and CsCl.[9] For solutions of other concentrations, the ε,φ curves were determined from these experimental curves

* Prof. L. Gierst kindly communicated to one of the authors that he no longer assumes that there is a difference in the n_1 values on the descending and the ascending branches, this question will be considered in more detail in Prof. L. Gierst's contribution to the discussion of the Rome CITCE meeting.

by making use of the condition of the invariance of ε at $\varphi - (RT/n_2F) \ln a_{\pm} = \text{const}$. The potentials are given in V and referred to N.C.E.

The determination of α_0 from the slope of the corrected Tafel plots for the reduction of H_3O^+, calculated from the data given in Ref. 10 and 11, leads to the value

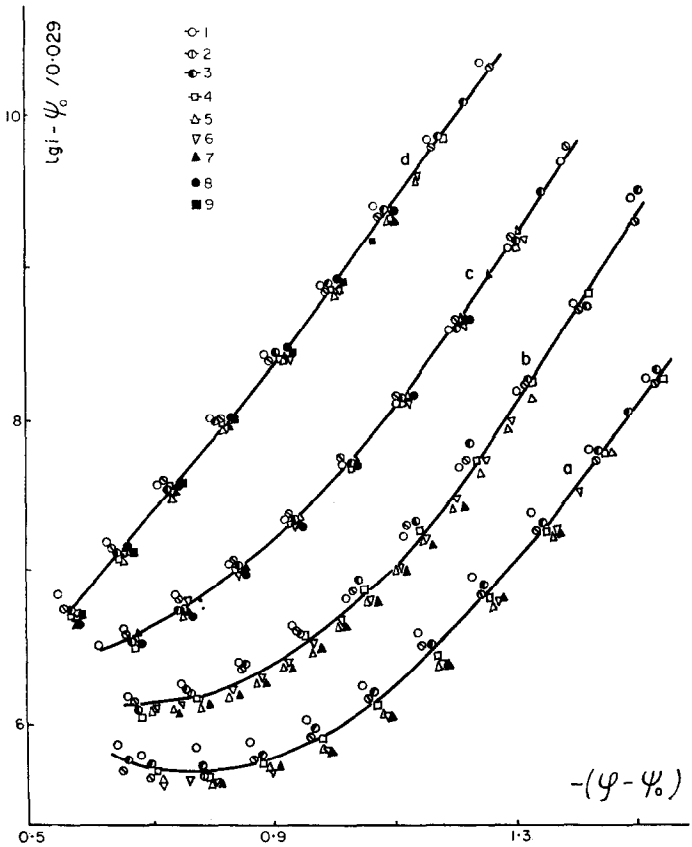

FIG. 3. Corrected Tafel plots of $S_2O_8^{2-}$ electro-reduction in solutions:
(a) 10^{-3} N $Na_2S_2O_8$: in the presence of LiCl + NaCl ($[Li^+]:[Na^+] = 10:1$) in concentrations 10^{-2} N (1); $1{\cdot}5 \times 10^{-2}$ N (2); 2×10^{-2} N (3); 3×10^{-2} N (4); 4×10^{-2} N (5); 5×10^{-2} N (6); 7×10^{-2} N (7).
(b) 10^{-3} N $Na_2S_2O_8$ in the presence of NaF in concentrations 3×10^{-3} N (1); 5×10^{-3} N (2); 7×10^{-3} N (3); 10^{-2} N (4); $1{\cdot}5 \times 10^{-2}$ N (5); 2×10^{-3} N (6); 3×10^{-3} N (7).
(c) 10^{-3} N $K_2S_2O_8$ in the presence of KCl in concentrations 2×10^{-3} N (1); 3×10^{-3} N (2); 4×10^{-3} N (3); 5×10^{-3} N (4); 6×10^{-3} N (5); 7×10^{-3} N (6); 8×10^{-3} N (7); 10^{-2} N (8).
(d) 10^{-3} N $Cs_2S_2O_8$ in the presence of CsCl in concentrations 0 (1); 5×10^{-4} N (2); 10^{-3} N (3); $1{\cdot}5 \times 10^{-3}$ N (4); 2×10^{-3} N (5); $2{\cdot}5 \times 10^{-3}$ N (6); 3×10^{-3} N (7); 4×10^{-3} N (8); 5×10^{-3} N (9).

$0{\cdot}50 \pm 0{\cdot}02$ with LiCl, KCl and CsCl as supporting electrolytes. The corrected Tafel plots practically coincide for various concentrations of supporting electrolytes.

The corrected Tafel plots for the reduction of $S_2O_8^{2-}$ on a dropping mercury electrode with LiCl + NaCl, NaF, KCl and CsCl of various concentrations as supporting electrolytes are shown in Fig. 3. An allowance for concentration polarization

was made according to Meiman–Bagotsky's theory[10]. The effect of the nature of the cation is noticed at once. For various cations the corrected Tafel plots lie in the same sequence, as the l vs. g i/φ curves at identical concentrations of the supporting electrolytes, but in the case of the corrected Tafel plots the differences are somewhat larger, since the ψ_0 values are more negative for CsCl solutions. For various concentrations of one and the same cation, the corrected Tafel plots coincide completely or approximately. The coincidence is better with CsCl and KCl as supporting electrolytes and much worse with LiCl, in which case the curves are as a rule located the lower, the greater the concentration of the supporting electrolyte. The coincidence improves with a rise of $-(\varphi - \psi_0)$. This coincidence could be regarded as a confirmation of the correctness of equating ψ_1 with the value ψ_0.[13] This conclusion, however, should be taken with a certain reserve. Indeed, from equation (6), which was deduced on the basis of the thermodynamic theory of electrocapillarity, by taking into account that at sufficiently negative potentials, the values of ψ_0 calculated by means of the theory of the diffuse layer satisfy the condition $\psi_0 = \text{const} + (RT/n_2F)\ln c$ at $\varphi - \psi_0 = \text{const}$, it is easy to obtain

$$\left\{\frac{\partial[\ln i + (n_1F/RT)\psi_0]}{\partial \ln c}\right\}_{(\varphi-\psi_0)} = 0, \tag{10}$$

whence

$$\ln i + \frac{n_1F\psi_0}{RT} = f(\varphi - \psi_0). \tag{11}$$

Thus, the coincidence of the corrected Tafel plots obtained at various c must be realized within the whole range of applicability of equation (6), i.e. at sufficiently low c and large $-\varphi$, irrespective of assumptions about the detailed mechanism of the process and about the structure of the double layer.

At very negative φ the corrected Tafel plots for the solutions investigated are rectilinear, and the value of α_0 determined from the slope of the straight lines is equal to $0{\cdot}30 \pm 0{\cdot}02$, which is in good agreement with that found by a different method in Ref. 1. The almost rectilinear shape of the corrected Tafel plots within the whole range of φ investigated is observed only upon the reduction of $S_2O_8^{2-}$ with CsCl as supporting electrolyte. With KCl, NaF and LiCl supporting electrolytes, a deviation from rectilinearity is observed on approaching the point of zero charge, which increases upon the transition from K^+ to Li^+. In the case of NaF, and especially LiCl, the minimum observed on the experimental log i vs. φ curves is retained on the corrected curves.

In the case of the reduction of $Fe(CN)_6^{3-}$ the corrected Tafel plots are turned with their concave side towards the $-\varphi$ axis (Fig. 4). The slope of the rectilinear sections of the curves in the range of large $-\varphi$ leads to $\alpha_0 = 0{\cdot}16$ for LiCl as supporting electrolyte (in agreement with the value obtained earlier[15,16]) to 0·17 for KCl and 0·19 for CsCl. In the initial section the corrected Tafel plot has a steeper slope in the case of CsCl as supporting electrolyte.

If we assume, as it is done in the deduction of equation (1), that by taking into consideration the value of ψ_0 it is possible in principle to determine correctly the dependence of the effective concentration of the anion on the potential and on the bulk concentration and that Tafel's equation must hold for the reaction of anion

reduction, the effective concentration of anions remaining constant, we can consider the reasons for the deviations of the corrected Tafel plots from rectilinearity. The appearance of a minimum on the corrected Tafel plots may be perhaps explained by a certain specific adsorption of $S_2O_8^{2-}$, which results in higher process rates in the vicinity of the point of zero charge than could be expected on the base of purely electrostatic concepts. Another factor not taken into consideration in the deduction of equation (1) is the discrete structure of the double layer. It is probable that to a very rough approximation it could be taken into account by considering separately the interaction of the anion with the next neighbouring cation, resulting in the form-

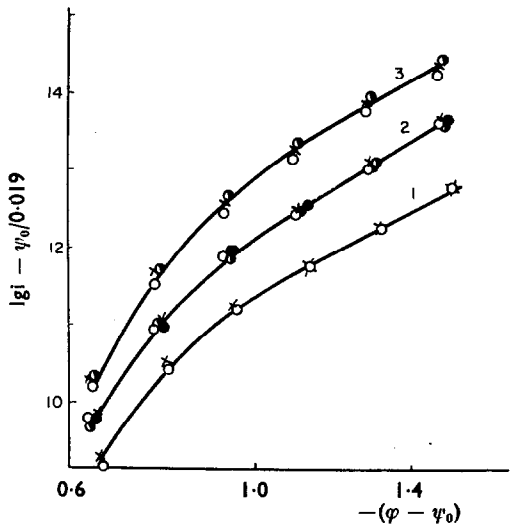

FIG. 4. Corrected Tafel plots of $Fe(CN)_6^{3-}$ reduction in solutions: (1) 10^{-3} N $Li_3Fe(CN)_6$ in the presence of LiCl in concentrations 10^{-3} N (× × × ×), 3×10^{-3} N (○ ○ ○ ○); (2) 10^{-3} N $K_3Fe(CN)_6$ in the presence of KCl in concentrations 0 (○ ○ ○ ○), 5×10^{-4} N (× × × ×), 10^{-3} N (◑ ◑ ◑ ◑), $1{\cdot}5 \times 10^{-3}$ N (● ● ● ●) (3) 10^{-3} N $Cs_3Fe(CN)_6$ in the presence of CsCl in concentrations 0 (○ ○ ○ ○), 3×10^{-4} N (× × × ×), 5×10^{-4} N (◑ ◑ ◑ ◑).

ation in the double layer of something like an ionic pair, and by using a ψ_0 value calculated by means of classical theory in order to take into account the action of other cations. As shown by the location of the corrected Tafel plots, the interaction with the neighbouring cation diminishes in the sequence $Cs^+ > K^+ > Na^+ > Li^+$. The fact that in the case of CsCl, the corrected Tafel plots approach rectilinearity can be explained as the result of mutual compensation of two effects: the decrease in the specific adsorption of $S_2O_8^{2-}$ with an increase in $-\varepsilon$ and the accompanying rise in the concentration of Cs^+ in the double layer. The role of the latter factor decreases in the sequence $Cs^+ > K^+ > Na^+ > Li^+$. This factor is the only one which determines the shape of the corrected Tafel plots of the reduction of the $Fe(CN)_6^{3-}$ ion, which is probably not specifically adsorbed at negative ε values and carries a high negative charge.

In the case of the reduction of $S_2O_8^{2-}$, the value α_0 was determined by other methods as well, which gave results in agreement with the conclusions from Fig. 3. The determination of α_0 by the graphical method of Gierst[2] is shown in Fig. 5. The curves

(a) connect the points corresponding to the condition $\psi_0 = \text{const}$. As follows from equation (9), the slope of these curves should be

$$-\left(\frac{\partial \lg i}{\partial \varphi}\right)_{\psi_0} = \frac{\alpha_0 F}{2{\cdot}3RT}$$

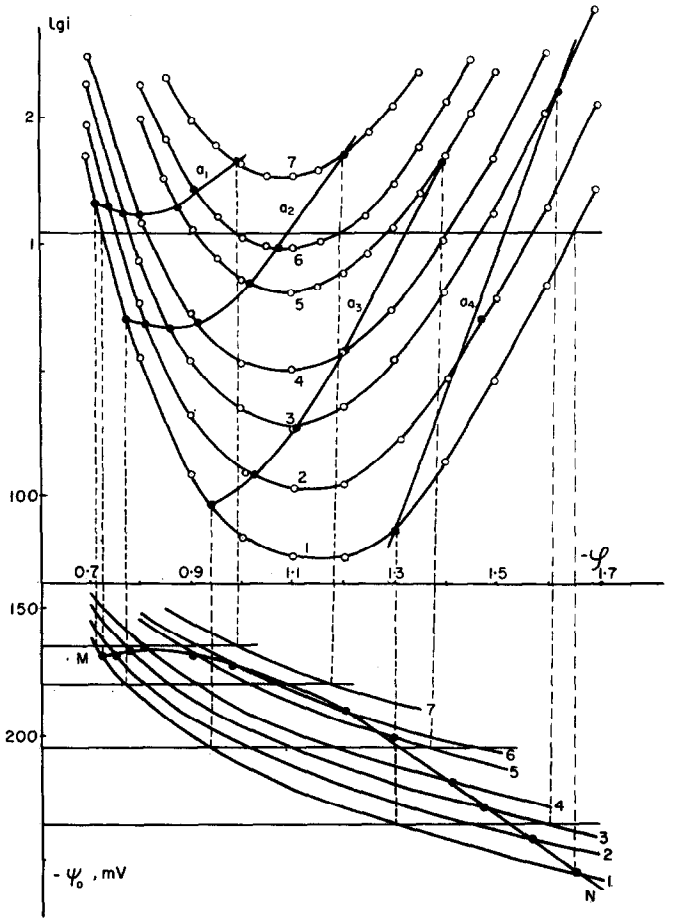

FIG. 5. Graphical analysis of the reduction curves of 10^{-3} N $Na_2S_2O_8$ in the presence of NaF in concentrations: (1) 3×10^{-3} N; (2) 5×10^{-3} N; (3) 7×10^{-3} N; (4) 10^{-2} N; (5) $1{\cdot}5 \times 10^{-2}$ N; (6) 2×10^{-2} N; (7) 3×10^{-2} N.

Actually the (a_1) and (a_2) curves have a small negative slope in the initial section, and only the (a_4) straight line leads to $\alpha_0 = 0{\cdot}30$ in the range of large $-\varphi$. The MN curve in the lower part of Fig. 5 represents the dependence of ψ_0 on φ at $\lg i = \text{const}$. At large $-\varphi$ there is a rectilinear section on the curve, the slope of which $(\partial\psi_0/\partial\varphi)_{\lg i} = \alpha_0/(-n_1 + \alpha_0)$ with $n_1 = -2$ also gives $\alpha_0 = 0{\cdot}30$.

We determined the dependence of the reduction rate of $S_2O_8^{2-}$ at $\varphi = \text{const}$. on $\psi_0 F/2{\cdot}3RT$, with NaF as supporting electrolyte, which is expressed by straight lines with the slope 1·6 at −0·75 V, 1·8 at −0·9 V, 1·85 at −1·1 V, 2·0 at −1·3 V, 2·2 at −1·5 V and 2·3 at −1·6 V. If equation (1) is satisfied, this slope should be equal to

$(-n_1 + \alpha_0)$. The results obtained by us are at variance with Gierst's conclusion,[2] according to which the $\lg i - (\psi_0 F/2{\cdot}3RT)$ dependence with NaF as supporting electrolyte has a slope of 2·0 on the descending and of 1·4 on the ascending branches of the i vs. φ curve. These results lead the authors to the conclusion that at large $n_1 = -1$ and $\alpha_0 \simeq 0{\cdot}4$. A graphical analysis of the data on the reduction of $S_2O_8^{2-}$ with CsCl as supporting electrolyte shows that the (a) and MN lines prove to be straight lines

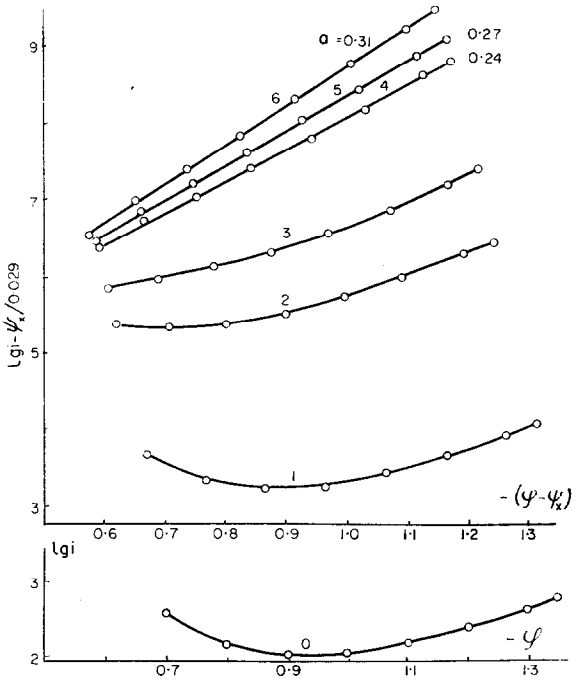

FIG. 6. Dependence of the reduction rate of 10^{-3} N $Cs_2S_2O_8$ in the presence of 2×10^{-3} N CsCl on the potential (0) and corrected Tafel plots, calculated on the assumption that the centre of the particle in the transition state is located at distance of 55·4 Å (1); 11·08 Å (2); 5·54 Å (3); 1·108 Å (4); 0·554 Å (5) from the outer Helmholtz plane, and on the latter (6).

practically over the whole range of potentials, except at more positive ones than −0·8, and lead to $\alpha_0 = 0{\cdot}30$. The slope of the straight lines in the co-ordinates $\lg i - (\psi_0 F/2{\cdot}3RT)$ equals to 1·65 at 0·7 V, 2·2 at −0·8 V, 2·2 at −0·95 V, 2·2 at −1·1 V, 2·3 at −1·25 V and 2·3 at −1·38 V.

Let us consider now the assumption according to which the centre of the charge in the transition state is located at some distance x from the outer Helmholtz plane in the diffuse part of the double layer. In Fig. 6 are shown the corrected Tafel plots of the reduction of 10^{-3} N $Cs_2S_2O_8$ in the presence of 2×10^{-3} N CsCl, calculated under this assumption for various x. The corresponding values of ψ_x were found by means of Gouy's theory. When the centre of the reacting particle is shifted from the Helmholtz plane in the direction of the solution, the slope of the corrected Tafel plot is at first gradually decreased. This change in the slope, however, is not great up to a distance of ~0·6 Å and lies within the experimental errors. At larger distances,

along with the decrease in the slope, a bend appears on the corrected Tafel plots. Thus, if it is supposed that the constancy of α is an indication of a real regularity, the assumption about the distances between the centre of the charge and the Helmholtz plane in excess of ~3–4 Å in the case of $S_2O_8^{2-}$ must be excluded.

It is possible to straighten out the corrected Tafel plots of $Fe(CN)_6^{3-}$ reduction assuming that the reaction occurs at a distance of ~10 Å from the Helmholtz plane. But in that case an improbably low value of $\alpha \simeq 0{\cdot}05$ is obtained.

If it is supposed that the centre of the particle in the transition state is localized in the inner part of the double layer, it is possible, as was shown in Ref. 3, to obtain the following relation between α_0 and the true value of α:

$$\alpha_0 = \alpha + \gamma(n_1 - \alpha), \tag{12}$$

where γ is the ratio of the distance between the centre of the charge in the transition state and the outer Helmholtz plane to the thickness of the Helmholtz layer. It follows from equation (12) that the corrected Tafel plot must remain rectilinear at $\gamma > 0$, if it is rectilinear at $\gamma = 0$. The value of the slope of the corrected Tafel plot must decrease, however, in the case of cations and increase in the case of anions. Thus, at $n_1 = 1$, $\alpha_0 = 0{\cdot}50$ and $\gamma = 0{\cdot}50$, the value of α amounts to 0·25. At $\gamma = 0{\cdot}08$, $n_1 = -2$ and $\alpha_0 = 0{\cdot}30$, the value of α already proves to be equal to 0·50; at $n = -3$ and $\alpha_0 = 0{\cdot}16$, the value of $\alpha = 0{\cdot}50$ can be obtained with $\gamma = 0{\cdot}097$. Thus, the determination of α to a great extent depends on the assumptions about the location of the centre of the charge in the transition state in the Helmholtz layer.

One may, however, produce some arguments in favour of the conclusion that at sufficiently negative φ the quantity γ cannot have appreciable positive values and that, consequently, the values of α_0 found from corrected Tafel plots at negative φ appear to be close to the true ones. These arguments are founded on a comparative analysis of the kinetics of the electroreduction of anions on mercury and on a thallium amalgam. In the case when neither the reacting substance nor the reaction product display any specific adsorption, the difference in the rates of the process at identical electrode potentials is due, according to the theory of slow discharge, to the difference in the values of ψ_1-potentials, which in their turn depend on the location of the point of zero charge.[17] With a shift of the point of zero charge towards negative values, the ψ_1-potentials at constant φ become less negative, which must result in an increase in the rate of anion reduction. A quantitative comparison of the kinetics of the reactions on mercury and on a thallium amalgam can thus be used as a criterion of the correctness of the calculation of the ψ_1 value in equation (1), and, consequently, in the determination of the value of α. The investigation of the reduction of the BrO_3^-, IO_3^- and CrO_4^{2-} anions on a thallium amalgam dropping electrode led Delahay and Kleinerman[18] to the conclusion about the existence of a fair agreement between the increase in the rate of the reactions, observed upon the transition from mercury to the thallium amalgam, and the slow-discharge theory.

We studied the electroreduction of $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ anions on a dropping thallium amalgam electrode with Tl-concentrations equal to 40, 26, 9 and 1%, and of the $PtCl_4^{2-}$ anion on a 40% Tl–Hg electrode.* The amalgams were prepared and analysed by the method described in Ref. 20. The zero charge point of 40% Tl–Hg determined from the position of the minimum on the curve of the differential capacity

* The first data on the reduction of $S_2O_8^{2-}$ on a Tl amalgam were obtained in Ref. 19.

C, observed in 10^{-2} N NaF, proved to be −0·925 V in agreement with Ref. 20 and 21. For amalgams of other concentrations the points of zero charge were not determined, the values given in Ref. 20 being used instead.

As it follows from the measurements carried out, in accordance with the shift in the point of zero charge, on the i vs. φ curves of the anions investigated the current decay is shifted towards more negative values with an increase in the Tl content in the amalgam, and the rate of the anion reduction increases.

It follows from the comparison of the curves of $S_2O_8^{2-}$ reduction on 40% Tl–Hg, corrected for the concentration polarization in accordance with Meiman–Bagotsky's

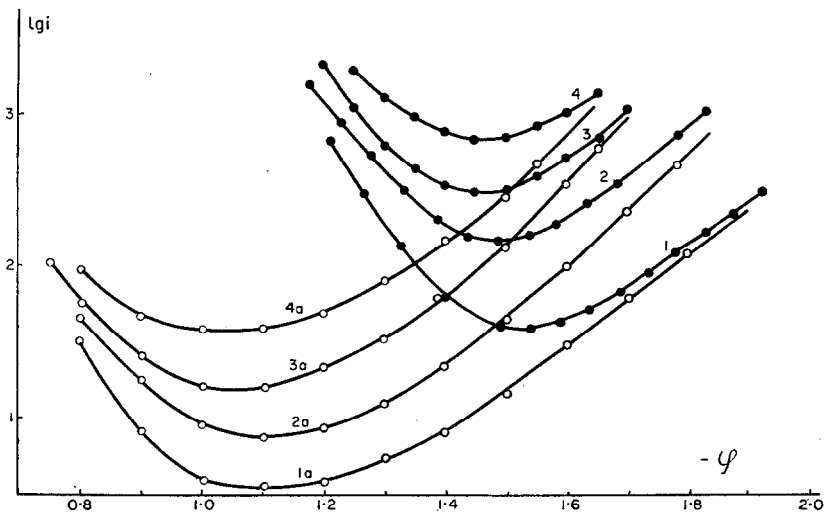

FIG. 7. Dependence of the reduction rate of 10^{-3} N $K_2S_2O_8$ on the potential on 40% thallium amalgam (● ●) and on a dropping mercury electrode (○ ○) in the presence of KCl in concentrations: (1) and (1a) 0; (2) and (2a) 10^{-3} N; (3) and (3a) 2×10^{-3} N; (4) and (4a) 4×10^{-3} N.

theory, with the corresponding curves for Hg, which is shown in Fig. 7, that the effect of an increase in the reaction rate depends to a great extent on the potential and at large $-\varphi$ becomes hardly noticeable. On 9% Tl–Hg the reduction rate of $S_2O_8^{2-}$ at $-\varphi > -1{\cdot}45$ V practically coincides with the reaction rate on mercury. This phenomenon can be explained taking into account the negative adsorption of Tl atoms on the amalgam surface at negative φ, which results in a decrease in the Tl concentration in the surface layer with a rise in $-\varphi$; in the case of an amalgam with a Tl concentration <10 per cent, the surface concentration at high $-\varphi$ values approaches zero.[21] The calculation of the curves of the dependence of the surface charge on the potential, by means of the data of Ref. 20, in comparison with the corresponding data for mercury, shows that the curves of the charge for both electrodes approach each other with an increase in $-\varphi$ and for 9% Tl–Hg practically coincide, beginning with $\varphi = -1{\cdot}5$ V.

A similar acceleration effect, decreasing with $-\varphi$, is observed also in the case of the reduction of $Fe(CN)_6^{3-}$ and $PtCl_4^{2-}$ anions. The inhibition of the reduction of $PtCl_4^{2-}$ is completely eliminated in the presence of 1 N KCl, whereas a narrow and deep minimum is retained under similar conditions on mercury.

The determination of the charge of the reacting particle by the method described on 40% Tl–Hg leads to $n_1 = -2$ in the case of $S_2O_8^{2-}$ and to n_1 values lying between -1 and -2 for the $PtCl_4^{2-}$ anion, as on a mercury electrode (with CsCl as supporting electrolyte).

For a quantitative comparison of the data obtained with the conclusions from the slow discharge theory, it is necessary to know the dependence of ψ_1 on φ and on the concentration of the supporting electrolyte. In the simplest case, it is possible to

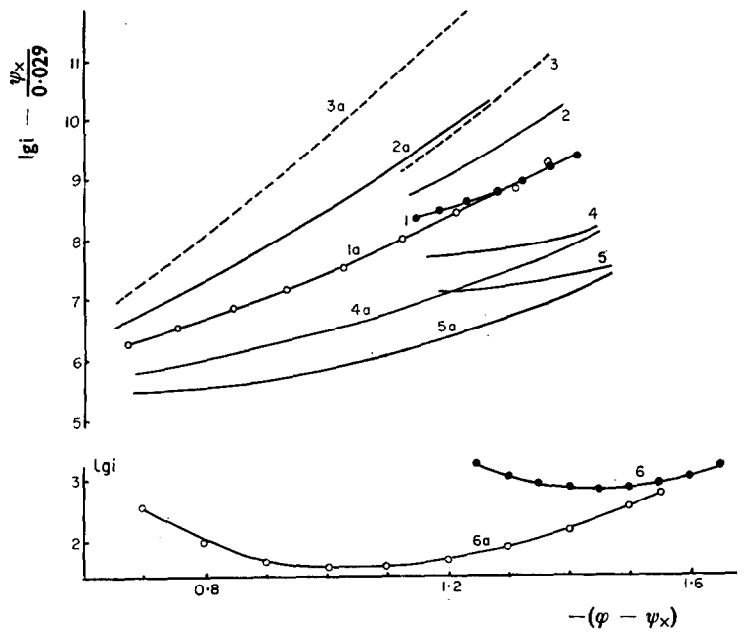

FIG. 8. Corrected Tafel plots of 10^{-3} N $K_2S_2O_8$ electro-reduction in the presence of 4×10^{-3} N KCl on 40% thallium amalgam and on a dropping mercury electrode (index a), calculated under the assumption that the centre of the charge of the transition state is located on the outer Helmholtz plane (1 and 1a), in the Helmholtz layer for $\gamma = 0{\cdot}05$ (2 and 2a) and $\gamma = 0{\cdot}10$ (3 and 3a) and at the distance of 2·16 Å (4 and 4a), and 4·32 Å (5 and 5a), from the outer Helmholtz plane. (6) and (6a) are the lg *i* curves on the amalgam and on mercury in one and the same solution.

assume $\psi_1 = \psi_0$. The calculation of the ψ_0-potentials was made by means of Grahame's method, using the C, φ curves for mercury and Tl amalgams obtained in Ref. 20. In this calculation, the effect of the negative adsorption of Tl on ψ_0 is automatically allowed for, since the latter affects the value of C. The values of ψ_0 found were used for the calculation of the corrected Tafel plots, which were compared with those for mercury. In the case of a quantitative agreement of theory with experiment, the curves for electrodes of different metals should coincide.

In the case of the $S_2O_8^{2-}$ anion, at negative φ the corrected plots coincide with those for mercury within 20–25 per cent for the 40% Tl amalgams (Fig. 8) curves 1 and 1a as well as for the 9% Tl amalgams. The difference observed at φ close to the zero-charge point of the amalgams may be caused, as well as the departure of the Tafel plots from rectilinearity, by a certain specific adsorption of the $S_2O_8^{2-}$ anion.

Upon the reduction of $Fe(CN)_6^{3-}$ and $PtCl_4^{2-}$, the corrected Tafel plots coincide in their shape and slope with those obtained on mercury, but they lie somewhat lower

than the latter. This means that the acceleration of the reduction of $Fe(CN)_6^{3-}$ and $PtCl_4^{2-}$ upon the transition to Tl–Hg proves to be somewhat lesser than it should be expected at $\psi_1 = \psi_0$. In the case of $PtCl_4^{2-}$, this is possibly caused by the difference in the adsorption conditions of the reaction product, Pt, on the surface of mercury and of the amalgam.

If it is assumed that the centre of the charge in the transition state is localized in the inner part of the double layer, the corrected Tafel plots of the amalgams in the case of the $S_2O_8^{2-}$ reduction are located appreciably lower than those for mercury, already if the distance of the centre from the outer Helmholtz plane equals to 4–5 per cent of the Helmholtz layer thickness (Fig. 8, curves 2, 2a and 3, 3a). Thus, the results of the comparison of theory and experiment, like the determination of α, to a great extent depend on the assumptions about the location of the centre of the activated complex in the Helmholtz layer. On the other hand, when the centre of the charge is shifted beyond the outer Helmholtz plane into the solution to distance up to $\sim$1 Å, (Fig. 8, curves 4, 4a,) the agreement between theory and experiment is not appreciably affected.* Thus, if in accordance with the slow-discharge theory, it is supposed that the corrected Tafel plots must coincide for electrodes from various metals, it is possible to draw the conclusion that in the case of anion reduction at negative φ the centre of the charge must be located either close to the outer Helmholtz plane or at small distances from it in the diffuse layer.

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* In the case of $Fe(CN)_6^{3-}$ reduction, when the centre of the charge is removed from the electrode surface, the coincidence of the corrected plots with those of mercury is improved and at the same time they are straightened, as has already been mentioned. The interpretation of this result necessitates, however, further investigations.