ZERO CHARGE POTENTIALS OF ELECTRODES*

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It is shown how the question as to the relation between the potential difference at the ends of a galvanic circuit and the Volta potential between metals in a vacuum could be solved by the introduction of the concept of the zero charge potentials of electrodes. Experimental methods for the determination of zero charge potentials in aqueous solution and in molten salts are reviewed. The influence of the zero charge potential on the electrochemical behaviour of metals is discussed.

The notion of the potential of zero charge

If a galvanic cell is to be considered as a reversible system, the potential difference set up at the ends of the circuit, as has been well known since the time of Gibbs and Helmholtz, can be determined from the free energy of the chemical reaction occurring when the current is passing. The importance of this thermodynamic approach cannot be overestimated. It has, however, essential shortcomings; it is confined to reversible systems, whereas reversibility is seldom encountered in practice, the deviation from it being the greater the higher the rate of processes occurring in the system. Moreover, the determination of the overall value of the potential difference at the ends of the circuit gives no indication as to the distribution of this potential difference between various interfaces, in particular, at the interphase between metal and solution, which is of greatest interest from the point of view of electrochemistry.

Let us consider the evolution of the views on the setting up of a potential difference at the metal/solution interface. A definite hypothesis on this problem was advanced in 1896 by Nernst.[1] To each metal he ascribed a certain solution tension P. If the osmotic pressure of ions in solution, p, is greater than P, the metal is positively charged upon contact with the solution, the ions from the solution being deposited on the metal. In the opposite case, ions of the metal pass into solution and the metal is negatively charged. In both cases, an electric double layer is formed at the metal/solution interface, since the charged surface attracts ions of the solution; at $p > P$ anions and at $p < P$ cations. According to Nernst, the potential difference between metal and solution, φ, is equal to $(RT/nF)\ln(p/P)$, which in the case of dilute solutions is in agreement with thermodynamics.

Nernst's osmotic theory leads to an important conclusion: the setting up of a potential difference should involve a change in the composition of the solution, proportional to the area of the metal/solution interface. This conclusion was experimentally confirmed in 1898 by the Swedish electrochemist W. Palmær.[2] Palmær constructed an effective dropping mercury electrode : under a pressure of 5 atm. mercury ran into dilute $Hg_2(NO_3)_2$. The mercury jet disintegrated into droplets, on whose surface mercury ions were deposited, since for mercury in $Hg_2(NO_3)_2$ $p > P$. Palmær actually found that during the operation of the dropping electrode the concentration of Hg_2^{2+} ions in the solution decreased by 39 per cent.

In Nernst's view, the potential difference at the interface between two metals could be neglected, i.e. in a galvanic circuit potential differences appear at the metal-electrolyte interfaces only. Hence it followed that by measuring the potential of the electrode for which $p = P$, it would be possible to determine the position of the absolute zero of the potential scale. Palmær's early work in Stockholm[3] was devoted to this problem. It is evident that for the condition $p = P$ to be fulfilled, the concentration of mercury ions in the solution should be greatly lowered. This was accomplished, e.g. by adding the complexing agent KCN. By varying the $Hg(CN)_2$ content in a 0.1 M KCl + 0.01 M KCN + 0.0008 M KOH + $Hg(CN)_2$ solution, Palmær determined the conditions under which the decrease of the mercury concentration in the solution during the operation of the dropping electrode changed to an increase. The solution in which the dropping electrode caused no change of concentration was called a null solution. The potential of a decinormal calomel electrode (D.C.E.) measured against the dropping mercury electrode in a null solution was equal to +0.5735 V. According to Palmær, this should be the absolute value of the potential difference between metal and solution in a D.C.E. In other words, the absolute zero potential should lie at −0.5735 V relative to the D.C.E. corresponding to −0.52 V relative to the normal calomel electrode (N.C.E.).

The experimental technique used by Palmær was excellent, but the interpretation of the result, based as it was on Nernst's assumptions, was incorrect. In fact, the quantity which changes to zero in Palmær's null solution is the charge of the electrode surface. Therefore, the value −0.5735 relative to the D.C.E. determines the position of the potential of zero charge or of the null point of mercury in the solution used in Palmær's experiment, practically 0.1 M KCl. Another question is, however, whether the potential difference at that point is zero. This must be answered in the negative. It is not possible to give here all the details of the historical development of this problem, important steps in it being the works of Paschen[4] and Rothmund[5], also on dropping mercury electrodes, that of Gouy on electrocapillarity,[6,7] and of Smith and Moss on null solutions.[8] Some experiments carried out by myself[9] at the very beginning of my scientific activity showed that in general no direct relationship exists between the value of the surface charge and the metal/solution potential difference. That not only the processes of ions transfer from one phase to another, but that also those of adsorption of molecules and ions contribute to the occurrence of potential differences, could have been concluded earlier, in the first instance on the basis of electrocapillary measurements made by the French physicist Gouy.[6,7] According to the thermodynamic Lippmann-Helmholtz equation

$$\partial\sigma/\partial\varphi = -\varepsilon \qquad (1)$$

the maximum of the electrocapillary curve, showing the dependence of the interfacial tension σ on the electrode potential φ should correspond to the zero value of the surface charge density, ε*.

The data of Gouy and other investigators clearly showed that, depending on

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* The meaning ascribed to the term "charge" in thermodynamic relations and in the electric double layer theory are somewhat different. I shall not dwell on this difference, however, as it is of no importance in most cases considered in this paper.

the composition of the solution, the maxima of the electrocapillary curves lie at different potentials and, in particular, shift in the direction of more negative values in the presence of surface-active anions. Many scientists, as for instance van Laar[10], however, believed that eq. (1), although deduced from thermodynamics, required corrections. When I began to work in this direction it seemed to me that in the first place it was essential to prove the validity of eq. (1) in all cases, regardless of the nature of the adsorption phenomena occurring in the solution. This was accomplished by analysis of the thermodynamic deduction of eq. (1) in some detail, as well as experimentally by comparison of values of $\partial\sigma/\partial\varphi$ determined from electrocapillary measurements with those obtained directly by means of a dropping electrode.[9] The results showed that the measurements by means of a dropping electrode on the one hand, and by a capillary electrometer on the other, should necessarily give the same value of the potential of zero charge, as was earlier established empirically for the particular case of inorganic electrolytes.[4,8] Consequently, in addition to the double layer due to the charging of the metal surface in the sense of Nernst, the double layers resulting from the adsorption of anions and from the adsorption and orientation of molecules should be taken into account as well.

The value found by Palmær for the zero charge potential of mercury is somewhat shifted by the adsorption of chloride ions. In the absence of adsorption of anions and surface active molecules, the potential of zero charge of mercury in aqueous solutions, according to the most accurate data,[11, 33] lies at -0.472 V relative to the N.C.E. or at -0.191 V relative to the normal hydrogen electrode (N.H.E.). It was natural to suppose that the orientation of solvent molecules should also be taken into consideration. This possibility was considered already by Gouy[12] and confirmed in experiments carried out by myself with non-aqueous solutions.[13] The complexity of the problem is not due solely to adsorption phenomena, however. In fact, a null solution can be obtained by a method different from that used by Palmær. For, instead of lowering the concentration of mercury ions it is possible to substitute for mercury an amalgam of a metal with a more pronounced ionization tendency. In this case, the null solution can be obtained at a much higher concentration of the potential-determining ions. This possibility was considered by Palmær, but he did not succeed in realizing it, which saved him from a disappointment. In fact, when I and my co-workers investigated the electrocapillary behaviour of thallium amalgams [14] and the properties of dropping electrodes from these amalgams,[15] a 0.5 M Na_2SO_4 + 0.00006 M Tl_2SO_4 solution proved to be the null solution for a 10 per cent Tl amalgam. But the zero charge potential in that case was equal not to -0.19 V as for mercury, but to -0.51 V vs. the N.H.E. For a 41.5 per cent Tl amalgam the value is -0.65 V. Some years later we determined the zero charge potential also for a platinum hydrogen electrode.[16] In that case the charging of the electrode occurs through the ionization of the adsorbed hydrogen atoms, which results in the acidification of the solution, or through the discharge of hydrogen ions, changing to atoms, this process leading to an alkalization. If the surface of a platinized electrode is large enough, the changes in the acidity caused by the formation of the electric double layer can be measured, and by altering the surface concentration of adsorbed hydrogen it is possible to determine the point of zero charge. We found that in 0.5 M Na_2SO_4 +0.005 M H_2SO_4 it is located at +0.11 V vs. the N.H.E., i.e. 0.3 V more positive than in the case of mercury and ca 0.8 V more positive than for the 41.5 per cent Tl amalgam.

Zero charge potentials and galvanic cells

The dependence of the zero charge potential on the nature of the metal leads to important conclusions. Let us consider an electrochemical cell

$$\underset{\text{Hg}}{1}\ \big|\ \underset{\text{null solution}}{2}\ \big|\ \underset{\text{null solution}}{3}\ \big|\ \underset{\text{Tl/Hg}}{4}\ \big|\ \text{Hg}$$

in which the null solutions contain no foreign ions or molecules adsorbed on uncharged mercury and amalgam surfaces. The sulphate solution mentioned above approximately meets this condition. As follows from the above, the potential difference at the ends of the circuit amounts to 0.46 V for a 41.5 per cent or 0.32 V for a 10 per cent amalgam. However, no ionic double layers or layers of oriented dipoles of adsorbed foreign molecules are present either at interface 1 or at interface 3; the potential difference at interface 2, as is well known, can be neglected or eliminated. If it is assumed, in addition, that the potential differences due to the orientation of water molecules at the interface with mercury and at that with the amalgam differ but little from each other — some arguments in favour of this assumption will be given below—the potential difference at the ends of our circuit proves to be quite similar to the Volta potential, or, as it is sometimes still said, to the contact potential between metals in a vacuum*. In fact, in the case of null solutions with non-adsorbed components, the principal difference between the metal-vacuum and the metal-electrolyte interfaces, consisting in the formation of double layers as a result of interaction of the metal with the solution components, has been eliminated (with the above reservation concerning the role of the solvent molecules). A direct measurement of the Volta potential between mercury and thallium amalgam confirms this conclusion (0.38 V for a 12 per cent amalgam).[17] Let us consider now a cell made up of a mercury electrode and an electrode from a 41.5 per cent thallium amalgam in normal solutions of corresponding salts. The potential difference at the ends of this circuit is 1.13 V. As follows from the above, 1.13—0.46 = 0.67 V is the algebraic sum of the potential differences localized in the ionic double layers, the remaining part being of the same nature as the Volta potential between metals in a vacuum.

Thus, the determination of the positions of the points of zero charge gives an answer to the question as to the relationship between e.m.f. of a galvanic cell and the Volta or contact potentials set up between metals in the absence of chemical interaction. This question is known to have arisen just after Volta's discovery at the end of the 18th century, and during the course of the whole 19th century the opinions of physicists and physical chemists on this question differed. Pfaff and Davy were in favour of the contact theory, Ritter, de la Rive and Faraday supported the chemical one. The great success of the thermodynamical theory of electromotive forces of reversible cells, which showed that the overall value of the potential difference at the ends of the circuit is completely determined by the nature of the chemical reaction occurring when the current is passing, made it natural to suppose that individual potential differences as well are set up only at metal-electrolyte interfaces at which a chemical interaction is possible. This point of view was embodied in Nernst's osmotic theory referred to above. How deeply the German physico-chemical school believed in the complete erroneousness of Volta's contact theory is shown by the words of

* The Volta (or contact) potential is the so-called outer electric potential.

W. Ostwald used in reference to it in *Elektrochemie, ihre Geschichte und Lehre*. "Wir stehen hier an einem Punkte (1797), wo der folgenreichste Irrtum der Elektrochemie beginnt, dessen Bekämpfung weiterhin fast den grössten Teil der wissenschaftlichen Arbeit auf diesem Gebiet in Anspruch genommen hat".

But not all physicists shared that opinion. Somewhat later, due to improvements in the vacuum technique, reliable data on the electron work functions could be obtained, which left no doubt as to the presence of a potential drop in the space between two metals upon their contact under vacuum in the absence of any chemical interaction:

$$\overline{\mathrm{Me_1 \mid vacuum \mid Me_2 \mid Me_1}}$$

As follows from thermodynamics, this Volta potential is equal to the difference in the electron work functions of both metals. The Volta potential can also be defined as the potential difference between the ends of the circuit:

$$\mathrm{Me_1 \mid vacuum \mid Me_2 \mid Me_1}$$

if the potential drop in the vacuum is eliminated. On the other hand the Volta potential between metals Me_1 and Me_2 is evidently equal to the difference in the surface potentials of metals Me_1 and Me_2, increased by the potential difference at the interface between the two metals or, to use a more modern term, the Galvani potential at the Me_2/Me_1 interface. The question naturally arises: what happens to these potential differences if an electrolyte solution is substituted for the vacuum? Perhaps it is these potential differences which are measured at the ends of the galvanic circuit? This point of view found expression in Langmuir's paper *The relation between contact potentials and electrochemical action*[18] in which he advanced the hypothesis that contact potentials were an essential, or perhaps even a major, part of the potential difference measured in electrochemical circuits. In a sense it was a return to Volta's original point of view, the main difference being that the data on Volta potentials were obtained from measurements made by using modern vacuum technique. Langmuir, however, did not consider either the question as to exactly which part of the potential difference in a galvanic circuit should be compared with the Volta potential, or in what way the required thermodynamic dependence of this potential difference upon the composition of the solution could be explained on the basis of the picture suggested by him. These questions can be solved by introducing the concept of the potential of zero charge; the difference between the potentials of zero charge of two metals determines that part of the total potential difference which can be compared with the Volta potential under vacuum. This part is superimposed by the potential differences in the electric double layers at the metal-solution interfaces, the dependence of which on the composition of the solution ensures the fulfilment of the thermodynamic requirements.[14, 19, 20]

As was pointed out above, the Volta potential between two metals is equal to the difference of the surface potentials of the two metals increased by the Galvani potential at the interface between them. In contrast to the Volta potential, it is impossible to determine these separate potential differences directly by experiment. I shall not dwell here on the problem of the determination of the separate or absolute, as they are sometimes called, potential differences between two points in different phases, e.g. in two metals, in a metal and a vacuum or in a metal and an electrolyte solution. Let us merely recall that in

order to determine such a potential difference, we have to measure the work performed during the transfer of an infinitesimal amount of electricity from one phase to the other, whereas in reality we have to deal only with the transfer of an electron or of ions. In this case the work performed during the transfer depends not only on the difference of electrical potentials, but also on the interaction of the particle with the material medium. This limitation is eliminated only in the case of two dilute solutions in the same solvent. However, although the values of separate potential differences cannot be measured directly, one may attempt to evaluate them on the basis of model concepts of the interface structure. Langmuir[18] supposed that the potential difference in the surface layers of metals at the interface with the vacuum could be neglected, or in other words, to use more modern terms, that the Volta potential and the Galvani potential between two metals were equal. Such an assumption is in complete agreement with Volta's concepts. Gurney[21] and Butler[22] held a similar view. It can be readily shown, however, that this assumption is incorrect and that the potential difference in the surface layer of metals is not to be neglected. In fact, the electron work functions on different faces of a metal crystal are known to differ. Consequently there must exist a certain Volta potential between two points in a vacuum located in the vicinity of these faces. Evidently this potential is completely determined by the potential difference at the metal-vacuum interfaces for both the crystal faces, since the mean potential at all points inside the crystal is constant. The cause of the setting up of the potential difference at the metal-vacuum interface was considered by Frenkel.[23] According to Frenkel the electronic gas which possesses a zero kinetic energy tends to expand and leave the confines of the lattice of positive ions until it reaches the limit where the potential difference set up compensates for the tendency of the electronic gas to expand. In principle these potential differences could be evaluated, and some attempts in this direction were made.[24,25] But it seems that the electronic theory of metals has not yet attained that degree of development at which the results of these calculations could be considered sufficiently reliable to solve the question of the values of the individual components of the Volta potentials (see also ref.[20]).

Experimental determination of zero charge potentials

Liquid electrodes in aqueous solutions

I have already mentioned the basic methods for the determination of the points of zero charge of liquid metals — the measurements of electrocapillary curves, the use of dropping electrodes and of null solutions. These methods are applicable in aqueous solutions to mercury, amalgams and liquid gallium. Examples of electrocapillary curves are given in fig. 1. From electrocapillary curves the value of the charge can be calculated with the help of eq. (1); dropping electrodes give the position of the point of zero charge and, under definite conditions, directly the value of the charge. If the charge was determined at some particular potential value, the charges at any other potential, and hence the position of the potential of zero charge, can be found by measuring and integrating over the differential capacity of the electrode. If follows from the thermodynamic eq. (1) that the results of the direct determination of the charge and those of its calculation from the dependence of σ on φ should coincide within experimental errors. It should be noted that sometimes eq. (1)

is considered to be inapplicable in the case of electrodes which are not "ideally polarizable".[26] In Palmær's experiments, however, the Hg electrode was not ideally polarizable due to the presence of mercury in the form of $Hg(CN)_2$ in the solution. Nevertheless, the potential of zero charge, determined by Palmær for 0.1 M KCl viz. — 0.52 V vs. N.C.E. is in excellent agreement with the results of electrocapillary measurements. Similarly, experiments with thallium amalgams show[15] that the determination of the potential of zero charge by the method of electrocapillary curves on the one hand, and using null solutions on the other, yield very similar values of the potentials of zero charge in spite of the fact that in the vicinity of the zero charge an amalgam electrode cannot be considered to be ideally polarizable since it is in equilibrium with the solution containing Tl^+ ions in a measurable concentration (ca 2×10^{-6} M in the case of a 41.5 per cent thallium amalgam[14]). This result is in complete agreement with the deduction of eq. (1) from Gibbs's adsorption equation,[9] which is a more general one than those based on the concept of an ideally polarizable electrode (see also ref.[27]).

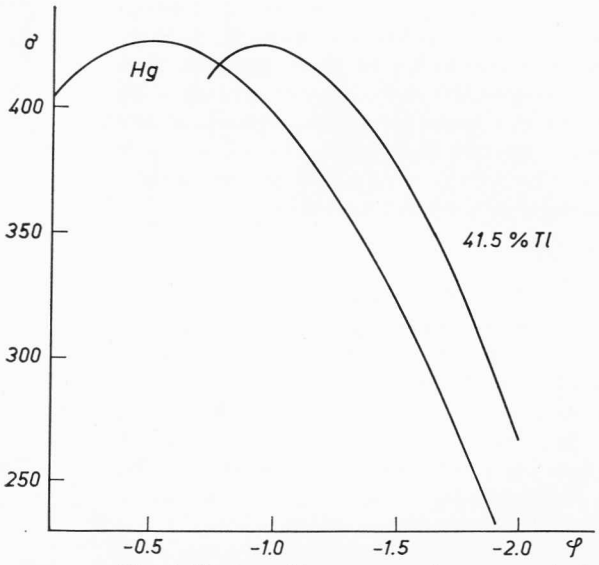

Fig. 1. Electrocapillary curves of mercury and of a 41.5 % Tl amalgam in 0.5 M Na_2SO_4; N.C.E. (Frumkin and Gorodetskaya[14]).

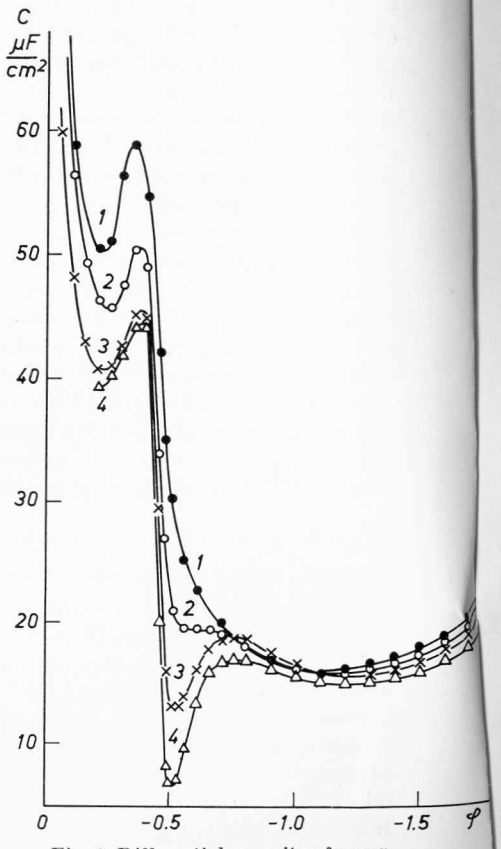

Fig. 2. Differential capacity of a mercury electrode in $K_4Fe(CN)_6$ solutions. N.C.E. (Damaskin, Swarz and Frumkin[34]). 1—N; 2—0.1 N; 3—0.01 N; 4—0.001 N. 25° C.

Another independent and non-thermodynamic method is based on the measurements of the differential capacity of the double layer in dilute solutions. According to the double layer theory the effective thickness of the diffuse double layer reaches its maximum value in the vicinity of the potential of zero charge. This corresponds to a minimum on the differential capacity curve.[28] The thickness of the diffuse double layer in the vicinity of the zero charge potential is often called the Debye thickness, although in reality it was Gouy's theory of the diffuse layer which was taken as a basis for the Debye-Hückel theory of strong electrolytes and not vice versa.

The results obtained by the determination of the potential of zero charge from electrocapillary curves and from the differential capacity minimum in dilute solutions agree well. This is the case not only with a practically ideally polarizable mercury electrode, but also with amalgam electrodes, for which the condition of ideal polarizability is not fulfilled. Thus the differential capacity minimum of the double layer for a 40 per cent Tl amalgam in 0.01 M NaF is located at -0.645 V (N.H.E.),[29] which is very close to -0.65 V, the potential of zero charge of a 41.5 per cent Tl amalgam in 0.5 M Na_2SO_4 determined from the electrocapillary measurements.[14, 15] The data obtained in 0.01 M NaF and 0.5 M Na_2SO_4 are quite comparable as the adsorption of anions may be neglected in both cases.

These results, as well as the coincidence of the data obtained by the method of null solutions with those of electrocapillary measurements, lead to the conclusion that in contrast to assertions made in the literature,[30, 31] there are no fundamental differences between the zero charge potentials of ideally polarizable electrodes and of electrodes in solutions containing potential-determining ions in a measurable concentration (see also ref.[32]).

The differential capacity curves with a minimum were first obtained with a mercury electrode in a 0.001 M KCl solution.[28] Fig. 2 gives an example of the relation between the differential capacity C and the electrode potential and shows the disappearance of the minimum at the point of zero charge with increasing concentration. The very sharp rise of the differential capacity observed in dilute $K_4Fe(CN)_6$ solutions, when the potential is shifted from the zero charge potential towards more positive values, is due to the high negative charge of the $Fe(CN)_6^{4-}$ anion.

Solid electrodes in aqueous solutions

Among the methods mentioned for liquid electrodes, only the determination of the potential of the differential capacity minimum can be directly applied to solid metals.[35] A number of such measurements were made at the Institute of Electrochemistry in Moscow with satisfactory results, e.g. in the case of Pb and Ag.[36] This method was also used by Randles in Birmingham.[37] Examples of differential capacity vs. potential curves obtained with solid electrodes are given in fig. 3 and 4.* The dependence of the differential capacity on the potential and on the concentration of the solution observed with some solid electrodes is similar to that observed with mercury. However, the interpretation of the double layer capacity measurements in the case of solid electrodes is hampered

* My thanks are due to Prof. J. B. Randles for the permission to present here the results of his measurements.

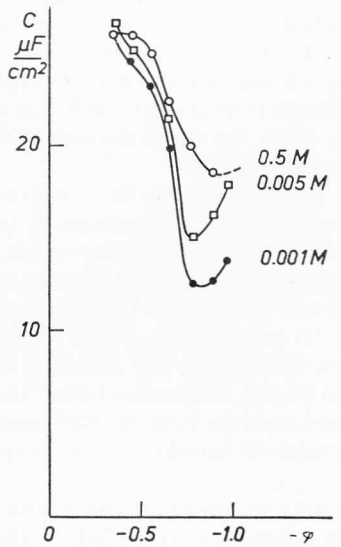

Fig. 3. Differential capacity of a silver electrode in Na_2SO_4 solutions; N.H.E. (Leikis[36]).

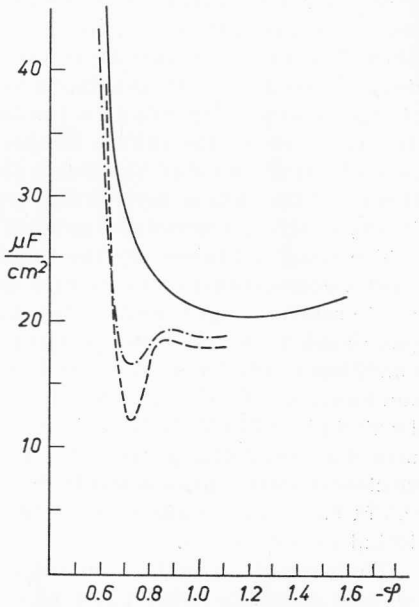

Fig. 4. Differential capacity of a tin electrode in $KClO_4$ solutions (Randles[37]) — 0.1 M; —.—., 0.01 M; — — — 0.001 M; pH ~ 3. N.C.E.

by the often observed dependence of the capacity upon frequency, the cause of which has not yet been completely ascertained.

There are no methods available which would permit us to make direct measurements of the interfacial tension between a solid metal and electrolyte and we cannot, therefore, determine an electrocapillary curve of a solid. Some measurable properties of solid metals, however, such as hardness, external friction and wetting, change with the potential in such a way as to make possible the determination of the potential of zero charge. Thus, the zero charge potential corresponds to the maximum hardness,[38, 39] to the maximum external friction[27, 40] (fig. 5) and to the minimum of wetting by electrolyte solutions.[41] The dependence of the wettability of a solid metal upon polarization was described as early as 1908 by Möller,[42] but incorrectly interpreted by him. It is of great importance for a number of problems of applied electrochemistry.

Just as the change in the composition of the solution in the case of the double layer formation on drops may be used for the determination of the potential of zero charge of mercury, the change in the composition when the double layer is formed on a solid with a highly developed surface, as I have already mentioned, may be successfully used for the determination of the zero charge potentials of activated carbon[43] or of platinized platinum.[16] These methods have lately been applied in our laboratory using radioactive tracers.[44] A direct measurement of the potential of a solid electrode with a developed surface under the conditions when the formation of the double layer is hindered or impossible, as in the case of an outgassed activated carbon electrode in an

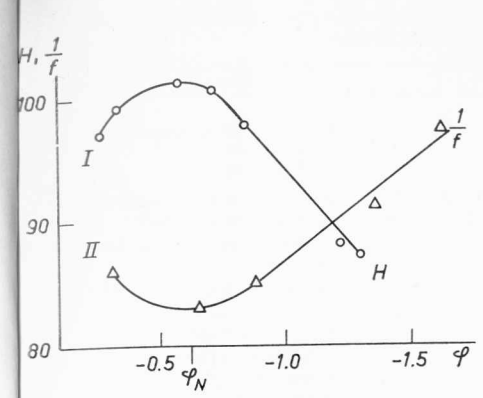

Fig. 5. Dependence of the hardness H and the external friction f of lead in 0.1 N NaCl on the potential; N.H.E. (Rehbinder, Wenström and Likhtman[38]).

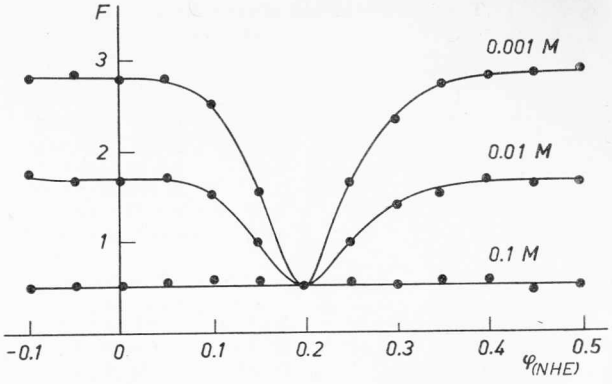

Fig. 6. Relationship between the potential and the force F, which must be applied in order to establish a contact between two platinum wires in KCl solutions. The minimum of F observed in dilute solutions corresponds to the point of zero charge (Voropaeva, Deryaguin and Kabanov[47]).

acid solution, is an analogue of the potential measurements with the help of an effective dropping electrode.[45]

Recently Jakuszewski suggested a method for the determination of the potential of zero charge based on the measurement in an electrolyte solution.[46] This shift, caused by the expenditure of electricity for the charging of the double layer, changes its sign at the potential of zero charge. The technique of these measurements is very simple, but the preliminary cleansing of the electrode surface should present considerable difficulties.

In addition to the determination of the position of the differential capacity minimum in dilute solutions, there are other methods, applicable to solids, in which the properties of the diffuse double layer are used, i.e. the potential distribution at some distance from the electrode surface. Among them the method of crossed wires[47] based on the measurement of the force necessary to overcome the repulsion of the electric double layers when two metal wires are brought together until they are in contact, should be mentioned (fig. 6), as well as the determination of the displacement of metal particles in an electric field (the electrokinetic or ζ-potential of colloid chemistry). The latter method was used a number of times for the determination of the sign of the surface charge of metals, often with contradictory results. It should be borne in mind that all forms of specific adsorption disturbing the potential distribution in the electric double layer will much more affect the ζ-potential than the value of the total charge ε. But, as exemplified by platinized platinum,[48] with certain precautions taken, the electrokinetic methods yield results in good agreement with those of adsorption methods. Conclusions regarding the position of the point of zero charge may also be drawn from the dependence of adsorption of organic compounds upon the potential[49, 50] and from the kinetics of electrochemical processes. Some data on the points of zero charge in aqueous solutions are listed in table 1.

TABLE 1. Potentials of zero charge in aqueous solutions referred to the standard hydrogen electrode. Starred (*) values are less reliable.

Electrode	$\varphi\varepsilon=0$	Electrolyte	Method
PbO_2	1.8	0.005 M H_2SO_4	Capacity minimum[36]
PbO_2	1.8	0.005 M H_2SO_4	Hardness[39]
Te	0.6*	0.5 M H_2SO_4	Hardness[38]
Au	0.3*	M $NaClO_4$ + 0.001 M $HClO_4$	Adsorption of organics[50]
C (act. carb.)	0.07	0.5 M Na_2SO_4 + 0.005 M H_2SO_4	Adsorption of ions[43]
C	0.16	0.005 M H_2SO_4	Potential outgassed electrode[45]
Pt(H)	0.11-0.17	0.5 M Na_2SO_4 + 0.005 M H_2SO_4; 0.025 M Cs_2SO_4 + 0.005 M H_2SO_4	Adsorption of ions[16, 44]
Pt(H)	0.2	0.001 M KCl	Crossed wires[47]
Pt(H)	0.12	0.000025 M H_2SO_4	Electrokinetic[48]
Cu	0.05*	0.1 M NaOH	Contact angle[52]
Cu	0.07*	0.01 M KCl	Dipping[46]
Hg	-0.19	0,01 M NaF	Electrocapillarity, dropping electrode[11]
Hg	-0.19	0.01 M NaF	Capacity minimum[33]
Bi	-0.36*	0.01 M KCl	Dipping[46]
Fe	-0.37*	0.005 M H_2SO_4	Capacity minimum[51]
Fe	-0.4*	0.003 M HCl	Crossed wires[47]
Sn	-0.46	0.001 M $KClO_4$	Capacity minimum[37]
Sn	-0.38*	0.01 M KCl	Dipping[46]
Ga	-0.61	1 M $NaClO_4$ + 0.1 M $HClO_4$	Electrocapillarity[76]
Tl/Hg 41.5 %	-0.65	0.5 M Na_2SO_4	Electrocapillarity[14]
In/Hg 58 %	-0.65	0.5 M Na_2SO_4 + 0.005 M H_2SO_4	Electrocapillarity[54]
Pb	-0.64 -0.67	0.0005 M K_2SO_4; 0.0005 M H_2SO_4	Capacity minimum[35, 36, 37]
Pb	-0.62	0.1 M NaCl	Hardness[38]
Ag	-0.7	0.0005 M Na_2SO_4	Capacity minimum[36]
Tl	-0.82	0.001 M KCl	Capacity minimum[35]
Tl	-0.69*	0.5 M Na_2SO_4	Hardness[38]
Cd	-0.9*	0.001 M KCl	Capacity minimum[35]
Na/Hg 0.3 %	-1.85*	0.1 M $N(CH_3)_4.1/2SO_4$ + 0.1 M NaOH	Dropping electrode[53]

The solutions used contained no foreign surface-active components and the composition of the electrolyte was chosen in such a way as to eliminate as far as possible the risk of a specific adsorption of anions.

At the present time, the zero charge potentials of solid metals can be determined within some hundredths of a volt, whereas the error in the determination of the zero charge potential of mercury does not exceed a millivolt. The principal difficulties encountered for many solid metals are due to the inhomogeneity of their surface, to the occurrence of various electrochemical processes and in many cases to the presence of adsorbed hydrogen and oxygen.

Liquid electrodes in molten salts

Of great importance for the expansion of our knowledge about the points of zero charge was the investigation of the electrocapillary properties[55] (fig. 7) and of the differential capacity[56, 57] of liquid metals (fig. 8) in molten electrolytes. Such investigations have been carried out for some years in the USSR at Sverdlovsk and Berezniaki as well as at the Institute of Electrochemistry in

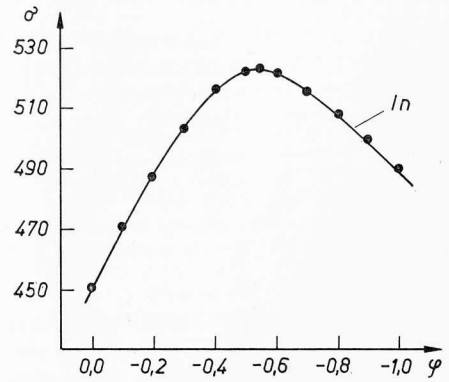

Fig. 7. Electrocapillary curve of molten indium in a LiCl + KCl melt at 450°. Reference electrode Pb, LiCl + KCl (Kusnetsov *et al.*[55]).

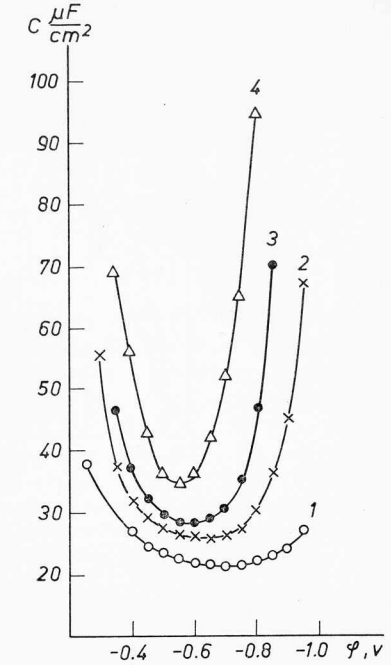

Fig. 8. Differential capacity of lead in KCl + LiCl melt 1—450°; 2—600°; 3—700°; 4—800°. Reference electrode Pb, 2.5 M $PbCl_2$, KCl + LiCl (Ukshe, Bukun and Leikis[56]).

Moscow. The technique of these measurements can now be considered to be thoroughly mastered, as shown by the agreement between the results of direct measurements of electrocapillary curves with the data obtained by double integration over differential capacity (fig. 9). The dependence of the interfacial tension and differential capacity on the potential in molten halides of alkaline metals proved in a sense to be simpler than in aqueous solutions, as the curves obtained are often approximately symmetrical with respect to the point of zero charge. At the potential of zero charge there is a minimum on the differential capacity curve, the nature of which, however, is essentially different from the capacity minimum in dilute electrolyte solutions. At 800° the capacity at the minimum is ca. 30 $\mu F/cm^2$ in K and Cs salt melts, and from 45 to 75, depending on the anion nature, in Li and Na salts. The minimum capacity increases with temperature by 3.3 $\mu F/cm^2$ per 100° in the case of K and Cs salts and by 11 $\mu F/cm^2$ in the case of Li and Na salts. The usual model of the double layer, in which the excessive charges are assumed to be localized in the Helmholtz layer, seems to be inapplicable for molten electrolytes. It may be supposed that the departure from uniformity in the distribution of charges under the action of the electric field penetrates into the melt at the depth of some atomic layers with the regions of opposite charge signs alternating.[57, 58, 59] Such a model was recently suggested for concentrated ionic systems by Stillinger and Kirkwood.[60]

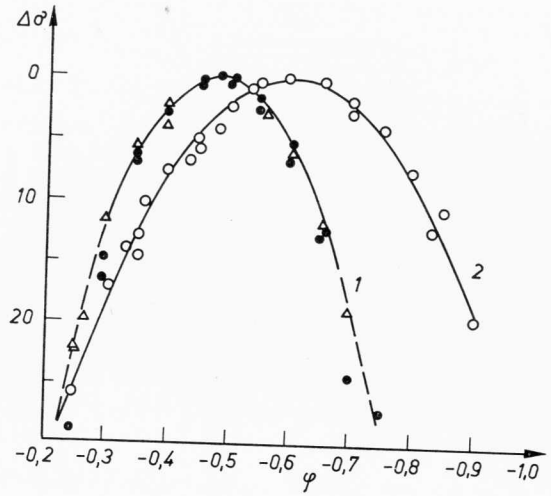

Fig. 9. Electrocapillary curves of lead in NaCl (1) and KCl (2) at 820° obtained by double integration of the differential capacity curves. Various kinds of dots correspond to experimental data (Ukshe, Bukun, Leikis and Frumkin[57]).

We can get an idea of the double layer structure if we suppose that the normal short-range order in the ionic melt is disturbed in a definite manner by the electric field of the metal surface charges.[61] In addition, while the behaviour of inorganic electrolytes at the interface with metals in aqueous solutions depends on the nature of the more weakly hydrated anions, in the melts the situation is different, the principal role being played by the cations owing to their smaller radii.

The molecular theory of the double layer structure in molten electrolytes is far from complete, but this is no obstacle to the use of the results of measurements of electrocapillary curves and of differential capacity for the determination of the points of zero charge. Often, dependence of the position of the point of zero charge on the nature of the metal is very pronounced. Some data obtained by these methods[55, 56, 57] are compared in table 2.

TABLE 2. Potentials of zero charge in molten salts (Pb, 2.5 % mol $PbCl_2$, KCl or KCl + NaCl, KCl + LiCl).

Electrode	$\varphi_{\varepsilon=0}$	t	Capacity minimum	t
Te	0.40	550°	0.40	550°
Sb	-0.20	750°	-0.17	700°
Hg	-0.23	400°		
Sn	-0.39	450°		
Bi	-0.48	420°	-0.32	700°
Ag	-0.50	1,050°	-0.32	700°
Ga	-0.50	700°	-0.62	1,000°
Ga	-0.57	450°	-0.60	700°
Pb	-0.58	750°	-0.65	450°
Pb	-0.70	450°	-0.55	700°
In	-0.67	450°	-0.72	450°
Cd	-0.82	450°	-0.82	700°
Tl	-0.85	420°	-0.80	700°
Mg			-0.87	700°
			-1.76	600°

TABLE 3. Potentials of zero charge referred to potential of zero charge of Pb.

	Aqueous solutions	Molten salts
Te	1.25	1.06
Hg	0.46	0.47
Bi	0.29	0.23
Sn	0.19	0.31
Ga	0.04	0.13
Ag	-0.05	0.01
Tl	-0.17	-0.15
Cd	-0.25	-0.12

Where a comparison is possible, an important conclusion may be drawn from these results: the potential difference of the zero charges in melts, as shown by table 3, proves to be close to that of zero charges in aqueous solutions. The comparison of the points of zero charge was made at as uniform a temperature as possible.

Contribution of zero charge potential differences to the galvanic cells

As we have now at our disposal some sufficiently reliable data on the points of zero charge, we can determine the contribution of different components to the total potential difference for some cells. In the case of a cell composed of Hg and a 41.5 per cent Tl amalgam in normal solutions of their respective salts, as was discussed above, 0.46 V of the total potential difference of 1.13 V consists of the difference in the potentials of zero charge. In the classical Weston cell the contribution of the difference in the zero charge potentials of mercury and Cd amalgam to the potential difference 1.018 V is ca 0.2 V. An interesting result is obtained in the case of a lead storage cell (the data refer, however, to 0.5 M H_2SO_4). The potential difference of the points of zero charge, 2.45 V, is not only comparable to that at the ends of the circuit, 2.03 V, but exceeds it. In fact, the potential of the negative Pb electrode, -0.35 vs N.H.E., is ca 0.3 V more positive than the point of zero charge, whereas the potential of the positive electrode 1.68 V is ca 0.1 V more negative than the point of zero charge of PbO_2. The lead surface is therefore charged positively and that of PbO_2 negatively. The determination of the dependence of the adsorption of cations and anions on the potential permits us to form an idea of the nature of the potential difference in the hydrogen-oxygen cell.[16, 44] In the case of a cell with platinum electrodes in 0,01 M CsOH the potential difference in the electric double layer practically does not contribute to the total potential difference since the adsorption of the cation but slightly depends on the electrode potential. The change in the latter, when the electrode is polarized, is primarily determined by the substitution of oxygen atoms for adsorbed hydrogen atoms and by the difference in the polarity of their bonds with Pt. In the case of the acid solution 0,005 M H_2SO_4 + 0,005 M Cs_2SO_4 until the potential of the positive electrode has attained the values at which the platinum surface starts to be covered with adsorbed oxygen, the major part of the total potential difference is localized in ionic double layers. However, a further shift of the potential in the direction of more positive values is accompanied not by an increase, but by a decrease in the positive surface charge and in the adsorption of the SO_4^{2-} anion. This is a result of the change in the potential of zero charge of platinum, caused by the appearance on the surface of adsorbed oxygen.

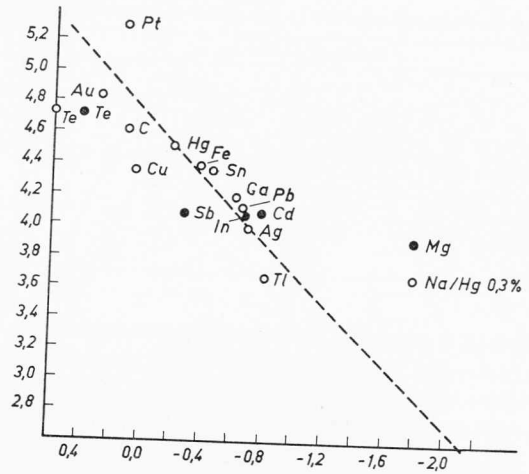

Fig. 10. Relation between the potential of zero charge $\varphi_{\varepsilon=0}$ (referred to N.H.E.) and the electron work function W_e. The values represented by full circles have been obtained in molten salts and recalculated on the N.H.E. scale assuming that the difference between the $\varphi_{\varepsilon=0}$ values in molten salts and in aqueous solutions are identical.

The zero charge potentials and the electron work function

As there are some data on the points of zero charge available, we can also compare on a larger scale the zero charge potentials with the electron work function W_e. If the vacuum Volta potential is equal to the difference of the potentials of zero charge, the latter should be a linear function of the electron work function with a slope of 45°:

$$\varphi_{\varepsilon=0} = W_e - 4.72 \qquad (2)$$

The constant in eq. (2) has been chosen so as to fit the values of $\varphi_{\varepsilon=0}$ and W_e for mercury, which are probably the most reliable ones. This conclusion is confirmed within certain limits by experiment, as can be judged from fig. 10. It should be noted that this comparison is difficult not only because of the inaccuracy in the determination of the points of zero charge, but in the first instance owing to the scattered values of the electron work function available in the literature. The values of W_e used in fig. 10 are those recommended in the latest collection of data on the electron work functions,[62] except the values for gold,[63] carbon[64] and the Na amalgam.[65] When the potentials of zero charge were determined in aqueous solutions, the conditions for the comparison of these two sets of values are in a certain sense unfavourable, as the determination of the electron work functions is made in high vacuum after a thorough outgassing of the metal and removal of oxide films. Moreover, the electron work functions are different for different crystal faces and until now the points of zero charge have been determined as a rule for polycrystalline materials. The comparison of contact potentials between liquid metals with the potential differences of points of zero charge in molten salts is more reliable, as in this case identical conditions of the determination of $\Delta\ \varphi_{\varepsilon=0}$ and $\Delta\ W_e$ were observed.

TABLE 4. Comparison of contact potentials and differences between points of zero charge, according to Kusnetsov *et al.*[66]

		Concentration of the 2nd component in the alloy in atomic %	Volta potential between metal and alloy	Difference of the potentials of zero charge of the metal and the alloy in KCl + NaCl
Sn	Sn + Te	0.15	-0.15	-0.18
Sn	Sn + Tl	23.8	0.17	0.24
Sn	Sn + Cd	53.0	0.25	0.27
Bi	Bi + Te	3.6	-0.30	-0.25
Bi	Bi + Te	9.0	-0.35	-0.33
Tl	Tl + Te	50.5	-0.65	-0.67

Table 4 shows that there is good agreement between the two sets of values. As the conclusion concerning the relationship between the potential of zero charge $\varphi_{\varepsilon=0}$ and the electron work function was recently discussed in the literature[67–70] I would like to emphasize that it is only of a semi-quantitative character. This limitation has no bearing on the experimental difficulties mentioned above, but is of fundamental significance. Let us first consider the case of aqueous solutions, although a similar conclusion holds in the case of molten salts. The limitation is connected with the necessity of taking into consideration the possible role of the solvent, water in our case, in the setting up of the potential difference at the metal-solution interface at the point of zero charge. There is no doubt about the existence of a certain potential difference in the surface layer of water at the interface with the gas phase. I shall not dwell here on the controversial question of its absolute value,[71] since this is not essential for the subsequent reasoning. It is important in our case that upon contact between water and mercury under conditions which preclude the formation of ionic double layers, the potential difference set up between water and mercury is not equal to the sum of potential differences at the water-gas and the vacuum-mercury interfaces. In fact the Volta potential in the system

mercury | indifferent gas | water | mercury

under conditions when the water-mercury interface is not charged, according to the most reliable measurements of Randles,[72] is equal not to zero but to 0.26 V. In other words, in addition to those already discussed, other processes occur upon contact between water and mercury, such as a reorientation of water dipoles, some of which become oriented with their negative ends towards the mercury surface,[19, 20, 73] or some change in the distribution of electronic density in the mercury surface layer under the influence of adsorbed water molecules.[74] The fulfillment of the relationship under consideration will evidently depend on the extent to which these effects may be assumed to be independent of the nature of the metal. This condition is probably fulfilled in the case of thallium amalgams, since the decrease in the interfacial tension upon transition from the metal-vacuum interface to the uncharged metal-water interface in the case of thallium amalgams is but little influenced by the concentration of the amalgam.[75] A more pronounced interaction between the water molecule and the metal surface than in the case of mercury is observed on the uncharged surface of liquid gallium,[76] which apparently leads to an additional shift in the point of zero charge towards more negative values. Thus

it will be correct to say that the difference of potentials of the zero charge expresses a certain Volta potential between two metals in a material medium, similar to the Volta potential in a vacuum, but not necessarily identical with it. However, judging from the fact that the potential differences of the points of zero charge in aqueous solutions and in molten salts differ but little, the effects of the nature of the medium and of the temperature are not large.

The influence of the potential of zero charge on the electrochemical behaviour of metals

In conclusion, I would like to consider the influence of the potential of the zero charge $\varphi_{\varepsilon=0}$ on the electrochemical behaviour of metals. At a definite value of the electrode potential φ the value of the charge and, hence, the potential distribution in the electric double layer, are determined by the quantity $\varphi - \varphi_{\varepsilon=0}$, i.e. by the potential read from the point of zero charge. This potential was called the rational electrode potential by Grahame[77]. Antropov, who discussed this problem in detail,[70] suggests the term "φ-scale" for a scale based on the points of zero charge. The rational potential φ_R was for the first time introduced in electrochemical kinetics when treating the problem of hydrogen overvoltage.[78] It is evident that the rational electrode potential φ_R or the potential on the "φ-scale" determines primarily the adsorption properties of the electrode. At positive φ_R the electrode adsorbs mainly anions, at negative φ_R cations; for adsorption of neutral molecules not too large absolute values of φ_R are most favourable.[79, 80]* Since the adsorption of substances is a necessary condition for their action on electrochemical processes, we must know the value of the φ_R potential in order to understand the effect of anions and surface-active additives on the processes of electrodeposition as well as on that of corrosion inhibitors.[70] Since the wetting of the electrode by water depends on the charge ε, the value of φ_R also largely determines the penetration of the solution into electrode pores[81] and the size of gas bubbles evolved during electrolysis.[82] I will confine myself here to consideration of the question of the form in which the potential of zero charge enters into the equations of electrochemical kinetics. For the sake of simplicity, let us suppose that we have to deal with an irreversible process of electroreduction of the first order with respect to the reacting particle, the electron transfer being the rate-determining step, that the coverage of the electrode surface both with the reacting particles and reaction products is small and that only coulombic forces are to be taken into account in the interaction between the reacting particles and the electrode surface. In this case, the current density i, expressing the process rate, in the absence of concentration polarization is determined by the equation:[78, 83–85]

$$\ln i = \alpha(-\varphi + g)\, F/RT + (\alpha - n)\,\psi_1\, F/RT + \ln c + \text{const} \qquad (3)$$

Here φ is the electrode potential measured against a constant reference electrode, α the so-called transfer coefficient ($0 < \alpha < 1$), g the non-coulombic part of the standard free energy of desorption of the reaction product from the

* This conclusion, however, is subject to essential limitations in the case of metals which appreciably chemisorb hydrogen and oxygen in contact with aqueous solutions. In this case the range of maximum adsorption of neutral molecules is determined not so much by the position of the point of zero charge, as by the minimum surface coverage with hydrogen and oxygen.[93]

electrode surface, c the concentration of the reacting particle in the bulk of the solution and n its charge. Of special importance is the quantity ψ_1, the potential at the point in the double layer in which the centre of the charge of the reacting particle in the transition state of the reaction is located. This equation was first suggested for the particular case of the hydrogen ion discharge on mercury.[78] According to eq. (3), at a given potential, φ, the nature of the electrode affects in the first instance the quantities g and ψ_1. The value of the constant seems to be but slightly dependent on it, at any rate the electron work function does not enter.[86, 87] The dependence of the hydrogen overvoltage on the nature of the metal is primarily determined by the quantity g and the effect of ψ_1 plays the role of an additional, although essential factor.

During the past fifteen years we have studied a number of reactions for which the quantity g may be neglected over a wide potential range, and the effect of the nature of the metal is determined primarily by the term with ψ_1.[83, 85, 88–90] These are electroreductions of anions, e.g. $S_2O_8^{2-}$, $Fe(CN)_6^{3-}$, MnO_4^-. Here both the reacting particle and the reaction product are negatively charged and are not adsorbed on the metal surface if its charge is negative enough. In addition, as n is negative, the coefficient before the term with ψ_1 is in this case large compared with that before φ, e.g. $2+\alpha$, as against α at $n = -2$. Therefore the term with ψ_1 greatly affects the shape of the polarization curve, which shows a decrease in the current density in the region of the transition from positive to negative surface charges due to the repulsion of the anion by the electrode surface, this decrease being followed by a rise at still more negative potentials. With an increase in the concentration and in the charge of the cations the negative value of the ψ_1 potential decreases and the current-voltage curves approach the usual limiting current density (fig. 11).

The location of the current decrease on the potential axis and hence the shape of the whole polarization curve for a solution of a given composition depend on the location of the point of zero charge. Fig. 12 shows the polarization curves of the $S_2O_8^{2-}$ reduction, obtained with rotating disk electrodes of gold, Hg (amalgamated copper), lead and cadmium.[90, 91] It can be seen that the expected

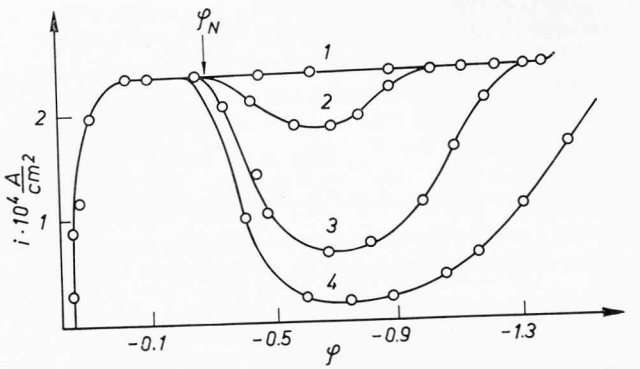

Fig. 11. Dependence of the current density on the potential in 0.0005 M $K_2S_2O_8$ with Na_2SO_4 additions. Amalgamated rotating disc electrode; 3.8 rps. Concentration of Na_2SO_4: 1—0.5 M; 2—0.05 M; 3—0.004 M; 4—0 (NCE) (Frumkin and Florianovich[83]).

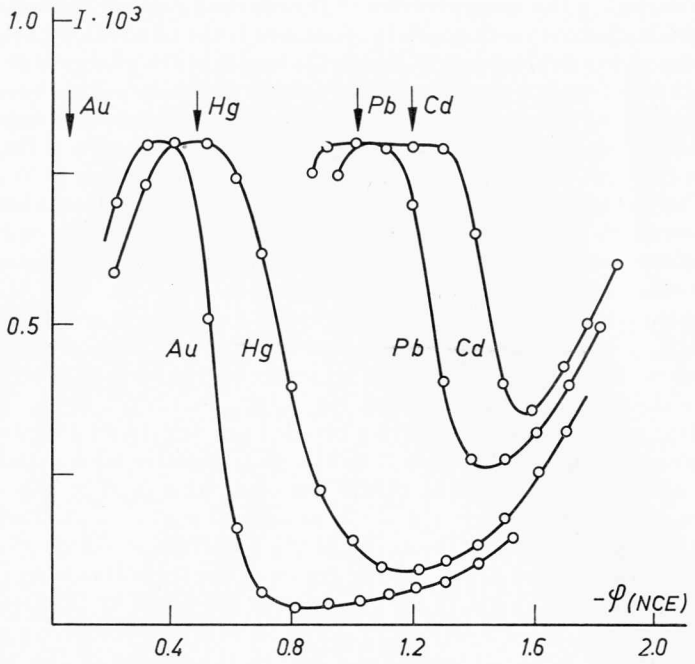

Fig. 12. Current-voltage curves of the $S_2O_8^{2-}$ reduction on different metals, 0.0005 M $K_2S_2O_8$ + 0.001 M KCl + 0.0002 M KOH. Rotating disc electrode. The arrows denote the potentials of zero charge (Nikolaeva-Fedorovich and Rybakov[91]).

relationship between the decrease in the current density and the position of the point of zero charge is observed.*

It follows from eq. (3) that the relationship between the values of ($\ln i + n\,\psi_1\,F/RT$) and (φ—ψ_1) for a given reaction when $g=0$ should not depend on the electrode material (corrected Tafel plots according to Delahay[92]). Examples of such corrected Tafel plots are given in fig. 13. The curves obtained for the reduction of $S_2O_8^{2-}$ on Hg and a 40 per cent Tl amalgam coincide; but in the case of Pb a marked difference is observed. This difference is probably due to the difficulty in determination of reliable values of ψ_1 for solid electrodes. The results obtained lately in the investigation of the electrocapillary properties of gallium[76] show, however, that this problem requires further study.

As already pointed out, the quantity φ in eq. (3) expresses the potential measured against a constant reference electrode. The presence of this term in the kinetic equation is the result of the increase in the gain of energy which occurs on electron transfer from the electrode to the reacting particle, with the potential shifting to more negative values, other conditions being equal. How

* In the case of neutral molecules or large organic ions whose adsorption changes the electric double layer capacity the position of the point of zero charge also affects the c.v. curve since it determines the surface concentration of the substance adsorbed. [79,80] This effect depends, however, not on $n\psi$, F, but on (C—C′) (φ—φ max)²/2 RT $\Gamma\infty$, where φ max is the potential of maximum adsorption, C- the Helmholtz double layer capacity and C′ the Helmholtz double layer capacity upon coverage of the surface with the adsorbed substance, $\Gamma\infty$ — the maximum adsorption.[94]

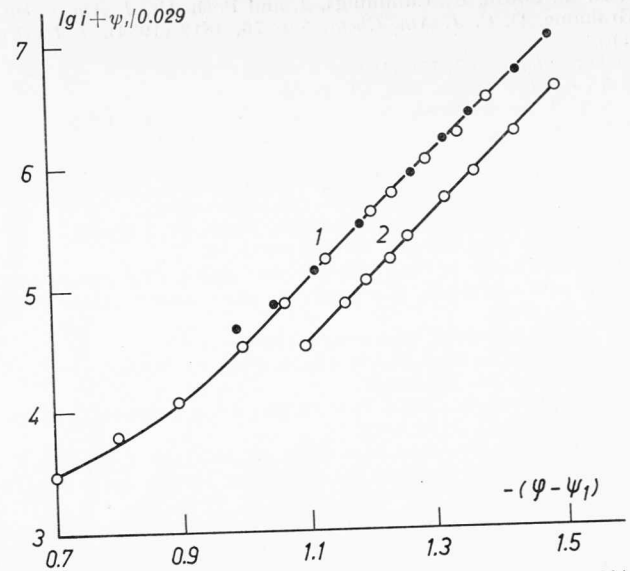

Fig. 13. Corrected Tafel plots for the reduction of $S_2O_8^{2-}$ (0.0005 M $K_2S_2O_8$ + 0.001 M KCl + 0.0002 M KOH). 1 — open circles-Hg; dots — 40 % Tl amalgam; 2-Pb (Nikolaeva-Fedorovich and Rybakov[91]).

this potential is realized is of no importance in this case. This term represents the connection between the kinetics of the electrode process and its thermodynamics, quite in the spirit of the chemical theory of galvanic cells. On the contrary, the term with ψ_1, referred to the point of zero charge, which appears as the result of an examination of the molecular mechanism of the process, depends not on its thermodynamics but on the structure of the interface and on the electronic properties of the metals. Both terms are equally necessary for a complete interpretation of the phenomena observed. Thus, a synthesis of the two opposite points of view is arrived at and we are reminded of the words of the great Swedish chemist, ". . . . nichts hat mich doch so gewundert, als dass Naturforscher gleichzeitig die elektrochemische Theorie annehmen und die Contakt-Elektrizität bestreiten ohne einzusehen, dass die eine nicht ohne die andere existieren kann".[95]

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