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POTENTIALS OF ZERO CHARGE, INTERACTION OF METALS WITH WATER AND ADSORPTION OF ORGANIC SUBSTANCES—II. POTENTIALS OF ZERO CHARGE AND THE WORK FUNCTION

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Abstract—The factors have been considered which can lead to a discrepancy between the difference of the potentials of zero charge and the difference of the work functions. It has been shown that some discrepancies are eliminated if instead of the potentials of zero charge, we compare the potentials corresponding to the same and sufficiently large negative electrode charge, thus ensuring the same interaction between the electrode surface and water dipoles. This method is however inapplicable to metal phases of variable composition if the *pzc* of their components differ significantly.

The analogy between the difference of *pzc* of two metals $\Delta\varphi_{\epsilon=0} = (\varphi_{\epsilon=0})_{Me_1} - (\varphi_{\epsilon=0})_{Me_2}$ and the Volta potential between them taken with the opposite sign $\psi^{Me_2Me_1} = W_{Me_1} - W_{Me_2}$ (W_{Me}—work function) was first pointed out in [1] when comparison was made of *pzc* of mercury and of concentrated thallium amalgams[2–4]. This analogy becomes evident if we compare the circuit Me_1 vacuum Me_2/Me_1 (Fig. 1a), in which the potential drop in vacuum is compensated for by the potential difference $\psi^{Me_2Me_1}$ applied from the outside, with the circuit in which vacuum is substituted by electrolyte solution, but both metals are at corresponding potentials of zero charge (Fig. 1b). In fact, in this case the main difference between the circuit formed by metals in vacuum and a usual galvanic circuit viz. the existence of ionic double layers at the metal/electrolyte interface, has been eliminated, but the metal surface in vacuum has been substituted by the metal surface in contact with electrolyte solution.

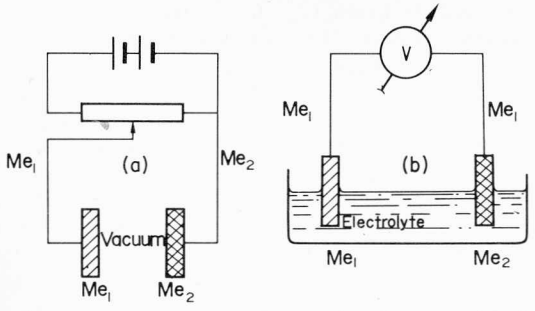

Fig. 1. Schematic diagram of the devices for measuring the Volta potential between the metals Me_1 and Me_2 (a) and for the determination of the potential difference between them in electrolyte solution at *pzc* (b).

The determination of the *pzc* of concentrated thallium amalgams and liquid gallium[5] has shown that the contribution of the Volta potentials to the value of the difference of potentials at the ends of a galvanic circuit can be very large.

The comparison of the value of $\Delta\varphi_{\epsilon=0}$ with that of the Volta potential is justified, no matter how the measured Volta potential is distributed between the surface potentials χ_{Me_1}, χ_{Me_2} (Galvani potentials metal-vacuum), which can not be measured directly, and the Galvani potential between two metals $g^{Me_2Me_1}$. However, it would be senseless if the difference of *pzc* were as a rule caused not by the potential jumps between the metals or in their surface layers, but by the difference in the orientation or in the dipole moment of water molecules at the surface of metal 1 and metal 2. It was pointed out in [1] that this supposition is improbable because the substitution of water molecules in surface layers by those of surface-active organic compounds (amyl alcohol, pyrogallol, thiourea) affects but slightly the value of $\Delta\varphi_{\epsilon=0}$.

It follows from Fig. 1a that

$$\psi^{Me_2Me_1} = W_{Me_1} - W_{Me_2} = \chi_{Me_1} - \chi_{Me_2} + g^{Me_2Me_1} \quad (1)$$

Taking into account a possible change of the dipole potential difference in the water surface layer[6], as well as the possibility of a change of χ_{Me} upon contact of uncharged metal with water[4,7,8], we obtain from Fig. 1b for $\Delta\varphi_{\epsilon=0}$:

$$\Delta\varphi_{\epsilon=0} = \chi_{Me_1} + \delta\chi_{Me_1} - (g_{dip}^{Me_1L})_{\epsilon=0} - \chi_{Me_2} - \delta\chi_{Me_2} + (g_{dip}^{Me_2L})_{\epsilon=0} + g^{Me_2Me_1} \quad (2)$$

where $(g_{dip}^{MeL})_{\epsilon=0}$ is the potential difference in the surface layer of the solvent in contact with metal at *pzc*, which

is usually associated with the orientation of its dipoles, assuming $g_{\mathrm{dip}}^{\mathrm{Me}L}$ to be positive, if the dipoles are turned with their positive end towards the solution, and $\delta\chi_{\mathrm{Me}}$ is the change of the surface potential of the metal upon contact of uncharged metal with water, assuming $\delta\chi_{\mathrm{Me}}$ to be positive, if χ_{Me} thereby increases.

Equation (2) ensues from the unambiguousness of the potential determination in the circuit in Fig. 1b. Combining it with relation (1), we obtain

$$\Delta\varphi_{\epsilon=0} = \psi^{\mathrm{Me_2Me_1}} - (g_{\mathrm{dip}}^{\mathrm{Me_1}L} - g_{\mathrm{dip}}^{\mathrm{Me_2}L})_{\epsilon=0} + (\delta\chi_{\mathrm{Me_1}} - \delta\chi_{\mathrm{Me_2}}) = \Delta W_{\mathrm{Me}} - \Delta(g_{\mathrm{dip}}^{\mathrm{Me}L})_{\epsilon=0} + \Delta\delta\chi_{\mathrm{Me}} \quad (3)$$

An equation equivalent to (3) can be found, *eg* in Trasatti's paper[9]. It expresses in an analytical form the necessity of introducing corrections into the relation between the difference of *pzc* and the Volta potential for the dependence on the metal nature of the orientation of solvent molecules and of the change of the electron density distribution in the metal surface, due to contact with solvent.

It is not difficult to obtain from Fig. 1b some more relations ensuring from the unambiguousness of the potential determination at a given point. Namely, it is evident that

$$\Delta\varphi_{\epsilon=0} = \psi_{\epsilon=0}^{\mathrm{Me_1}L} - \psi_{\epsilon=0}^{\mathrm{Me_2}L} + \psi^{\mathrm{Me_2Me_1}} = \Delta\psi_{\epsilon=0}^{\mathrm{Me}L} + \psi^{\mathrm{Me_2Me_1}} = \Delta\psi_{\epsilon=0}^{\mathrm{Me}L} + \Delta W_{\mathrm{Me}} \quad (4)$$

where $\psi_{\epsilon=0}^{\mathrm{Me}L}$ is the Volta potential between metal and solution at *pzc*[10]. Assuming that the value of $\psi_{\epsilon=0}^{\mathrm{Me}L}$ is not affected by the solvent adsorbed on the nonimmersed part of the metal surface*, we can write further

$$\psi_{\epsilon=0}^{\mathrm{Me}L} = -\chi_{\mathrm{Me}} + (\chi_{\mathrm{Me}} + \delta\chi_{\mathrm{Me}}) - (g_{\mathrm{dip}}^{\mathrm{Me}L})_{\epsilon=0} + \chi_L = \delta\chi_{\mathrm{Me}} - (g_{\mathrm{dip}}^{\mathrm{Me}L})_{\epsilon=0} + \chi_L \quad (5)$$

where χ_L is the surface potential of the solvent.

If follows from (5)

$$\psi_{\epsilon=0}^{\mathrm{Me}L} = \delta\chi_{\mathrm{Me}} - \delta\chi_L \quad (6)$$

if $\delta\chi_L$ is understood to be the value of $(g_{\mathrm{dip}}^{\mathrm{Me}L}) - \chi_L$, *ie* the change in the surface potential of solvent upon contact with uncharged metal.

According to (4), for a quantitative agreement between the difference of *pzc* of two metals in any solvent and the difference of work functions, it is necessary and sufficient that the Volta potential between metal and solution at *pzc* should be independent of the metal nature†. If $\delta\chi_L$ is taken to be zero, *ie* if we assume the dipoles orientation to be unchanged when passing from the free solvent surface to the interface with uncharged metal and ignore $\delta\chi_{\mathrm{Me}}$, then it follows from (6) that the Volta potential metal–solution disappears at *pzc* and in accordance with (4), the difference of *pzc* of two metals in any solvent is exactly equal to the Volta potential at the interface between them.

Butler was the first to consider the deductions from the assumption that the Volta potential between metal and solution at *pzc* is zero. Under this condition the Volta potentials measurements can be used for determination of *pzc*[19]. Although Butler himself observes that the assumption of the Volta potential between metal and solution at *pzc* being zero is at variance with the data of electrocapillary measurements, we find it time and again in later works, *eg* in the review of Perkins and Andersen[12] and in the monograph of Bockris and Reddy[13]; it was also used in attempts to prove theoretically the exact equality of the quantities $\psi^{\mathrm{Me_2Me_1}}$ and $\Delta\varphi_{\epsilon=0}$[14, 15]‡. However, the quantity $\psi_{\epsilon=0}^{\mathrm{Me}L}$ can be measured and the direct measurement shows the erroneousness of the assumption of its being equal to zero. Thus in [6] from the Volta potential measurements of Klein and Lange[16] the value $\psi^{\mathrm{HgH_2O}} = -0{\cdot}33$ was obtained§. The more accurate measurements of the Volta potential at the mercury/electrolyte solution interface carried out by Randles[11] together with Grahame's value for $(\varphi_{\epsilon=0})_{\mathrm{Hg}} = -0{\cdot}47$ *vs nce* led to the value of $\psi_{\epsilon=0}^{\mathrm{HgH_2O}} = -0{\cdot}26$. If $\psi_{\epsilon=0}^{\mathrm{Me}L}$ were equal to zero, the difference $\psi_{\epsilon=0}^{\mathrm{Me}L_1} - \psi_{\epsilon=0}^{\mathrm{Me}L_2}$ for two different solvents should be also zero. Experi-

* This condition was probably realized in the experiments of Randles[11], who used a dropping mercury electrode.

† This relationship was pointed out by Novakovsky, Ukshe and Levin[41].

‡ It is not difficult to understand why this assumption seemed to be natural. In fact, it is necessary for the appearance of the Volta potential between metal and solution that there should be free charges on their surfaces and since by definition at the metal–solution interface at *pzc* there occurs no charge exchange, it would seem that there is no source for such free charges. The erroneousness of this concept can be most simply shown taking as an example the contact of two electrolyte solutions of the same composition differing only in that the surface of solution 1 is clean and that of solution 2 covered, *eg* with a palmitic acid film. Let us suppose that the contact of the solutions through a porous diaphragm is achieved in such a manner that the surfaces of both solutions should lie in the same plane, being separated however by a barrier impermeable to palmitic acid. Since palmitic acid alters the surface potential of water by ~400 mV, in spite of the identical composition of solutions, the electrochemical potentials of dissolved ions differ before contact. They should become equal after it, which can be ensured only by the appearance of a Volta potential $\psi^{L_1L_2}$ between the surfaces of both solutions, which satisfies the condition $\psi^{L_1L_2} = \chi_{L_2} - \chi_{L_1}$. The setting up of an equilibrium Volta potential is realized due to the transition of charges of any nature from the surface of solution 1 to that of solution 2. Owing to the small capacity of the capacitor formed by the surfaces of solutions 1 and 2, the amount of these charges is negligible as compared with that exchanged by the two phases when the equilibrium Galvani potential is established (at the barrier width 1 cm by 7–8 orders of magnitude less). In the general case it should be borne in mind that when electrochemical equilibrium is attained between two contacting phases, charge exchange should ensure not only the establishment of an equilibrium Galvani potential, but also that of an equilibrium Volta potential.

§ Henceforth it is expedient to substitute for the designations Me and *L* the corresponding chemical symbols.

ment shows that this is not the case. In fact, determining the differences of the potentials $\Delta\varphi_{\mathrm{I}}$ and $\Delta\varphi_{\mathrm{II}}$ at the ends of the circuits

nce	aqueous solutions	air	nonaqueous solution (L)	aqueous solution	*nce*

(I)

and

nce	aqueous solution	Hg at $\epsilon = 0$	nonaqueous solution (L)	aqueous solution	*nce*

(II)

we obtain from (5)

$$\Delta\varphi_{\mathrm{II}} - \Delta\varphi_{\mathrm{I}} = \psi^{\mathrm{Hg}L}_{\epsilon=0} - \psi^{\mathrm{HgH_2O}}_{\epsilon=0}. \qquad (7)$$

For solutions in dimethylformamide the calculation by means of this equation according to the data of [17] gives $-0{\cdot}37$ V, and for solutions in methanol according to [18] $-0{\cdot}27$ V. Thus, taking $\psi^{\mathrm{HgH_2O}}_{\epsilon=0}$ equal to $-0{\cdot}26$ V, we obtain for the Volta potentials at the interfaces between uncharged mercury and dimethylformamide (DMF) and methanol resp. $\psi^{\mathrm{HgDMF}}_{\epsilon=0} = -0{\cdot}63$ V and $\psi^{\mathrm{HgCH_3OH}}_{\epsilon=0} = -0{\cdot}53$ V.

Equation (6) as applied to water can be written as

$$\psi^{\mathrm{MeH_2O}}_{\epsilon=0} = \delta\chi_{\mathrm{Me}} - \delta\chi_{\mathrm{H_2O}}. \qquad (8)$$

According to (8), if the surface potentials of metal and water remained unchanged upon their contact or changed by the same quantity, $\psi^{\mathrm{MeH_2O}}_{\epsilon=0}$ would be zero.

Since our knowledge of the value of χ_{Me} is very limited, especially in the case of metals for which *pzc* can be determined, historically the attention was centered on possible changes of $\chi_{\mathrm{H_2O}}$ upon contact with metal, primarily with mercury. Trasatti[9] tried to substantiate the validity of such an approach, assuming that though $\delta\chi_{\mathrm{Me}}$ is not equal to zero, it should not depend on the metal nature*.

The estimation of $\delta\chi_{\mathrm{H_2O}}$ should be based on that of $\chi_{\mathrm{H_2O}}$, *ie* on the value of the potential difference at the interface between water and the gas phase. This, as any determination of an individual potential difference, must be based on some model. An exhaustive treatment of this problem is beyond the framework of this paper. It should be noted only that the estimation of $\chi_{\mathrm{H_2O}}$ followed two different courses: on the basis of the interpretation of the results of the investigation of the adsorption phenomena and the determination of the temperature coefficient of χ[23–25, 51] on one hand, and the comparison of the experimentally found real hydration energies of ions G_r[11, 16, 27] and the calculated chemical ones G_{ch}. The calculation of G_{ch} was based on model representations of the interaction between ions and water (such calculation were first performed by Verwey[28], for later works see [29]), or on certain assumptions about the relationship between the hydration energies of cations and anions[27], which is in principle the same. While from considerations of the first kind a small positive value of $\chi_{\mathrm{H_2O}}$ $\sim 0{\cdot}1$ V seemed to be likely, the comparison of the experimental values of G_r and the calculated ones of G_{ch} led as a rule to negative values of $\chi_{\mathrm{H_2O}}$ equal to some $0{\cdot}1$ V [24, 30]†. A small positive value of $\chi_{\mathrm{H_2O}}$ seems to us to be more likely, but the question of the value of $\chi_{\mathrm{H_2O}}$ is to be considered still unsettled.

The uncertainty of the value of $\chi_{\mathrm{H_2O}}$ makes it difficult to interpret the physical sense of the value of $\psi^{\mathrm{HgH_2O}}_{\epsilon=0} = -0{\cdot}26$. As it follows from (8), this value can be accounted for both by a positive value of $\delta\chi_{\mathrm{H_2O}}$ and by a negative one of $\delta\chi_{\mathrm{Hg}}$. It was suggested in [6] that the negative value of $\psi^{\mathrm{HgH_2O}}_{\epsilon=0}$ is determined by the positive value of $\delta\chi_{\mathrm{H_2O}}$. In other words, it was assumed that the orientation of water molecules existing on the free water surface, at which the negative ends of dipoles are turned towards the gas phase, increases upon contact with mercury. However the comparison of the changes of $\chi_{\mathrm{H_2O}}$ and $\varphi_{\epsilon=0}$ in the case of adsorption of aliphatic compounds with one polar group from their aqueous solutions makes this conclusion questionable. Let us consider as an example the thoroughly investigated case of aliphatic alcohols. The similarity of their adsorption behaviour at the water/air and water/mercury interfaces[31] testifies to the same orientation of molecules at both interfaces. The comparison of the limiting shift of $\chi_{\mathrm{H_2O}}$ when passing from the surface layer of pure water to the layer filled with oriented aliphatic alcohol molecules, with that of $\varphi_{\epsilon=0}$, showed that beginning with C_2 up to C_6 the shifts of $\varphi_{\epsilon=0}$ are approximately by $0{\cdot}06$ V less than those of $\chi_{\mathrm{H_2O}}$[32]. This leads one to suppose that $g^{\mathrm{HgH_2O}}_{\mathrm{dip}}$ is not greater, but rather somewhat less, than $\chi_{\mathrm{H_2O}}$. This conclusion is supported by the comparison of the potential difference shifts during adsorption of organic substances oriented with a negatively charged atom outwards with respect to the aqueous phase (iodoalkyls)[24]. Hence $g^{\mathrm{HgH_2O}}_{\mathrm{dip}}$ probably is $\lesssim 0{\cdot}1$ V. The estimates of

* One of the main arguments is the supposed quantitative agreement between ΔW_{Me} and $\Delta\varphi_{\epsilon=0}$ when $\Delta\varphi_{\epsilon=0}$ is measured in molten salts. However, as is clear from the data of Kuznetsov *et al.*[20] and Ukshe *et al.*[21], this agreement is only approximate, though the discrepancies between the two series of values are probably somewhat less than in the case of determination of $\varphi_{\epsilon=0}$ in aqueous solutions. Since according to Trasatti, in molten electrolytes $\delta\chi_L$ is zero, then from the supposed agreement of ΔW_{Me} and $\Delta\varphi_{\epsilon=0}$, according to (6), we could conclude that $\delta\chi_{\mathrm{Me}}$ is independent of the metal nature. It is not clear, however, whether $\delta\chi_L$ is really zero in the case of molten electrolytes and why it should be so. It should be also borne in mind that apart from the fundamental reasons of the discrepancy between ΔW_{Me} and $\Delta\varphi_{\epsilon=0}$ considered here, this discrepancy can be also due to different pretreatment of metal surfaces in the determination of the two quantities. The latter is less if electrochemical measurements are performed at high temperature, particularly so, if both series of experiments are carried out with molten metals[22].

† Free energy hydration calculated recently by Dogonadze and Kornyshev on the basis of a theory of polar liquids developed earlier[60] and using radii of Gourary and Adrian[61] are consistent with $\chi_{\mathrm{H_2O}}$ $\sim 0{\cdot}0$ V[62].

$g_{dip}^{HgH_2O}$ in literature, based on these or other model representations, agree with this conclusion[33, 34]. Hence it also follows that the value of $\delta\chi_{Me}$ in (8) is positive.

As has been already pointed out in part 1[35], the interest in the problem of the dependence of $g_{dip}^{MeH_2O}$ on the metal nature arose in connection with the investigation of the electrocapillary properties of gallium[36, 37]. It follows from the determination of the *pzc* of gallium that $(\Delta\varphi_{\epsilon=0})_{HgGa} = 0{\cdot}50$ V. At sufficiently negative charges, the ϵ,φ dependences for Hg and Ga become parallel, but the distance between these parallel branches is only 0·17 V. This result was explained by the reorganisation of the electric double layer caused by the turning of the adsorbed water dipoles with their negative end towards the gallium surface when its negative charge decreased. Hence it was evident that the quantity $W_{Hg} - W_{Ga}$ should be compared with the distance between the negative branches of the ϵ,φ curves equal to 0·17 V, rather than with the shift of *pzc* when passing from Hg to Ga, equal to 0·50 V. To verify this conclusion, some measurements were performed, the results of which are listed in Table 1.

Table 1

$W_{Hg} - W_{Ga}$ (vacuum)	0·30[38]; 0·15[39]
$W_{Hg} - W_{Ga}$ (dielectric)	0·16 ± 0·06[40]*
$(\varphi_{\epsilon=0})_{Hg} - (\varphi_{\epsilon=0})_{Ga}$ (water)	0·50[36, 37]
$(\varphi_{\epsilon=q})_{Hg} - (\varphi_{\epsilon=q})_{Ga}$ (water)	0·17[36, 37]†
$(\varphi_{\epsilon=0})_{Hg} - (\varphi_{\epsilon=0})_{Ga}$ (KCl + LiCl, 400°)	0·35[20]

* On the basis of the measurements of the space charge-limited currents (dielectric-copper phtalocyanine).

† The comparison of the difference of work functions with the difference of potentials of the same negative charges for the couple Hg–Ga is justified, as at sufficiently negative ϵ the differential capacities of these two metals are practically the same.

where q stands for a sufficiently large negative value, *eg* 15 or 18 $\mu C/cm^2$.

It is clear from Table 1 that the measured values of ΔW_{HgGa} and of the *pzc* shift in molten salts are less than that of the *pzc* shift in water, but, except the values obtained in [39, 40], larger than the values of the shift of the negative branch of the electrocapillary curves (0·17 V). This fact precludes from making a final quantitative conclusion about the value of the change of $g_{dip}^{MeH_2O}$ when passing from mercury to gallium, although the qualitative conclusion about the preferred, as compared to mercury, orientation of water dipoles with their negative end towards the gallium surface is confirmed.

The development of the investigation of the quantitative relation between $\varphi_{\epsilon=0}$ and W_{Me} was as follows*. Novakovsky, Ukshe and Levin[41] found that the data at their disposal fitted best the relation

$$\varphi_{\epsilon=0} = 1{\cdot}02W_{Me} - 4{\cdot}88$$

being very close to a relation

$$\varphi_{\epsilon=0} = W_{Me} - 4{\cdot}78,$$

which they deduced assuming $\psi_{\epsilon=0}^{MeL}$ to be constant. A similar equation with a somewhat modified value of the constant in the right hand side was later many times compared with the experimental data, *eg* as in [22], where, however, its semiquantitative nature was emphasised

$$\varphi_{\epsilon=0} = W_{Me} - 4{\cdot}72. \qquad (9)$$

The value of the constant 4·72 was chosen in accordance with the data obtained for mercury.

According to Argade and Gileadi[42], equation (9) is valid. A somewhat different relation between $\varphi_{\epsilon=0}$ and W_{Me} was deduced earlier from experimental data by Vasenin[43]. According to Vasenin,

$$\varphi_{\epsilon=0} = 0{\cdot}86\,W_{Me} - 4{\cdot}25.$$

The difference from unity of the coefficient before W_{Me} Vasenin explained by the dependence of the orientation of adsorbed water molecules on metal nature.

An attempt to refine the relation between $\varphi_{\epsilon=0}$ and W_{Me} was made by Trasatti[9]. Having selected the most reliable, in his opinion, values of W_{Me}[44], Trasatti comes to the conclusion that the W_{Me}, $\varphi_{\epsilon=0}$ dependence can not be expressed by a linear relation valid for all metals. According to Trasatti, for *sp* metals, except Ga and Zn (Sb, Hg, Sn, Bi, In, Pb, Cd, Tl) to the first approximation

$$\varphi_{\epsilon=0} = W_{Me} - 4{\cdot}69$$

which almost does not differ from (9), whereas for transition metals (Ti, Ta, Nb, Co, Ni, Fe, Pd) to the same approximation

$$\varphi_{\epsilon=0} = W_{Me} - 5{\cdot}01.$$

In choosing the values of $\varphi_{\epsilon=0}$ for metals not adsorbing hydrogen, Trasatti favours those obtained from the position of the minimum on the differential capacity curve, however not always taking proper account of the fact whether the conditions ensuring the reliability of these data are satisfied[35]. In the case of platinum group metals Trasatti uses the *pzc* values obtained by the method of Eyring *et al.*[45] in neutral solutions,

* We thought it necessary to dwell in more detail on the history of the question since errors are often found in its treatment in literature. Thus, in [12] and [58] it is affirmed that the relation between *pzc* and work function in [1] was deduced from experimental data. Actually, the authors of [1] had at their disposal only the electrocapillary curves of thallium amalgams and the work function of thallium amalgams was first determined in [53], that is 15 yr after the appearance of [1]. See also [59].

Table 2

Metal	$(\Delta\varphi_{\epsilon=0})_{HgMe}$	$(\Delta\varphi_{\epsilon=q})_{HgMe}$*	$W_{Hg} - W_{Me}$
Au	−0·37	~ −0·37	−0·28
Sb	−0·04	—	−0·06
Bi	0·10	0·17	0·21
Sn	0·20	0·10	0·15
Ga	0·50	0·17–0·18	0·2
In	0·46	0·34 (corr.)	0·42
In–Ga	0·43 (CH_3CN)	0·33–0·34 (H_2O, corr.) 0·34–0·35 (CH_3CN)	
Ga–Tl†	0·51	0·40	
Tl	0·51	—	0·48
Pb	0·37	0·36	0·32
Cd	0·56	0·35	0·38

* $q = -18\ \mu C/cm^2$.
† According to [57].

believing that, unlike the *pzc* values obtained from the adsorption measurements, these refer to the metal surfaces free of adsorbed gases. However, the surface renewal without electricity supply from outside in the presence of a solvent—water, at best can ensure the vanishing of the total charge, but not that of the free charge*. In view of the above mentioned facts, in our opinion, the *pzc* values used by Trasatti for transition metals are not reliable enough.

Trasatti believes that it is possible to deduce a relation between $\varphi_{\epsilon=0}$ and W_{Me} covering all metals if account is taken of the dependence of $(g_{dip}^{MeH_2O})_{\epsilon=0}$ on the metal nature, considering, as has been pointed out above, the value of $\delta\chi_{Me}$ constant. This relation is of the form

$$\varphi_{\epsilon=0} = W_{Me} - 4{\cdot}61 - 0{\cdot}40\alpha \qquad (10)$$

where α is the degree of orientation of water molecules, which according to Trasatti increases in the sequence Au, Cu < Hg, Ag, Sb, Bi < Pb < Cd < Ga. Judging by the data on the adsorption of organic compounds considered in part I [35], the energy gain upon wetting of the uncharged surface with water increases indeed in the sequence Hg < Bi < Sb < Pb < Cd < Ga. We think that it is too early as yet to choose places in this sequence for Cu and Ag.

In this paper we have tried to extend the method used earlier for mercury and gallium to all metals whose behaviour was considered in part I[35], *ie* instead of comparing the values of ΔW_{HgMe} with those of $(\Delta\varphi_{\epsilon=0})_{HgMe}$, to compare them with $(\Delta\varphi_{\epsilon=q})_{HgMe}$, where q has a possibly large negative value, assuming that at sufficiently negative potentials water molecules are orientated similarly, so that at the same surface charge we consider the values of $(g_{dip}^{MeH_2O})_{\epsilon=q}$ and $\delta\chi_{Me}$ to be independent of the metal nature. Unlike in [9, 47], we shall not use here any definite picture of the arrangement of water dipoles, because the S-like shape of the water adsorption isotherm at mercury indicates that the layer of adsorbed water molecules in the case of uncharged or slightly charged metal surface is not that of dipoles arranged in parallel[48]. The shape of the adsorption isotherm of aliphatic compounds dissolved in water also testifies to the fact that the area per individual particle in the water monolayer is not 12·3 Å, as is supposed in [9], but two–three times more[48, 55].

Such comparison is expedient only in the case if the capacities of the dense layer of the metals being considered are the same, for otherwise the same charges will not correspond to the same potential drops in the dense layer. As can be seen from Fig. 2 of part I[35], at $q = -18\ \mu C/cm^2$, this condition is practically fulfilled for this whole group of metals, except In. As it follows from the data obtained in [49], this condition is fulfilled for the liquid In + Ga alloy if we compare the ϵ,φ curves for Hg and In + Ga measured not in water but in acetonitrile. We have used this fact for the determination of the value of $(\Delta\varphi_{\epsilon=q})_{HgMe}$ for this alloy. Unfortunately, data for In in acetonitrile are absent as yet. However, the value of $(\Delta\varphi_{\epsilon=q})_{HgMe}$ for In + Ga can be obtained using another method, viz. by allowing for increased capacity of In + Ga by a 10 per cent reduction of the experimental value of ϵ. After this correction of the ϵ,φ curve of In + Ga, it becomes parallel to the ϵ,φ curve of mercury at sufficiently negative potentials. The distance between the ϵ,φ curve of mercury and the corrected ϵ,φ curve of In + Ga is within the experimental error the same as that obtained in the experiments in acetonitrile (0·35 and 0·34, respectively)[49]. Taking into consideration the similarity of the surface properties of In and In + Ga[56], we used the ϵ,φ

* The choice of the values obtained in neutral unbuffered solutions is not very fortunate either, since continuous surface renewal used in those investigations could possibly have changed the solution pH. The values of *pzc* given in [45] for Pt metals in acid and alkaline solutions agree well with the results of adsorption measurements[46].

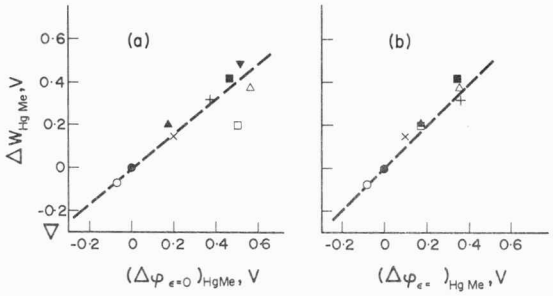

Fig. 2. Comparison of the dependences of the differences of the work functions for mercury and the given metal with those of the corresponding potentials of zero (Fig. 2a) and identical negative charges $q = -18\ \mu C/cm^2$ (2b). ▽ Au, ○ Sb, ● Hg, × Sn, □ Ga, ▲ Bi, + Pb, △ Cd, ■ In, ▼ Tl.

curve of In corrected in the same manner (reduction of ϵ by 10 per cent) for determination of the value of $(\Delta\varphi_{\epsilon=q})_{HgIn}$. The values of $(\Delta\varphi_{\epsilon=0})_{HgMe}$ and $(\Delta\varphi_{\epsilon=q})_{HgMe}$ for the metals considered are compared in Table 2, which contains also data for gold, because quite reliable results seem to have been obtained now for $\varphi_{\epsilon=0}$ of polycrystalline gold[50]. Taking into account the strong hydrophobic nature of gold[9, 50], we can assume that the value of $(\Delta\varphi_{\epsilon=0})_{HgAu}$ practically does not differ from that of $(\Delta\varphi_{\epsilon=q})_{HgAu}$. The values of $\varphi_{\epsilon=0}$ necessary for calculation have been taken from Table 1 in [35], and the values of $\varphi_{\epsilon=q}$ have been obtained by integration of the C,φ curves given also in [35], Fig. 2.

As can be seen from the Table 2, the differences between the values in the first and second columns are especially large for cadmium and gallium. Figure 2 shows the dependences of ΔW_{HgMe} on $(\Delta\varphi_{\epsilon=0})_{HgMe}$ and $(\Delta\varphi_{\epsilon=q})_{HgMe}$, respectively. To avoid a personal approach to the choice of the values of ΔW_{HgMe}, these are taken from the same list of data (Table 1 in [9]), which seemed to be the most reliable to the author of [9] and was not subjected by him to any corrections. An exception is made only for Ga, viz. the value 0·2, the mean of the three latest determinations[38–40], (see Table 1, according to [9] $\Delta W_{HgGa} = 0{\cdot}25$) being taken for ΔW_{HgGa}. It is seen from Fig. 2 that the experimental values of ΔW_{HgMe} fall somewhat better on a straight line with the slope 45°, if the values of $(\Delta\varphi_{\epsilon=q})_{HgMe}$ are plotted on the abcissa instead of those of $(\Delta\varphi_{\epsilon=0})_{HgMe}$, which supports the assumption about the necessity of taking account of $g_{dip}^{MeH_2O}$ when considering the relations between *pzc* and the function. The reliability of the comparison is however limited by the insufficient accuracy of determination of the work functions.

In conclusion, we would like to emphasize that care should be taken in using the values of $(\Delta\varphi_{\epsilon=q})_{HgMe}$, because the electric field of the double layer arising at large negative ϵ values, which is supposed to ensure a water molecules orientation independent of metal nature, can produce other changes in the interface structure too. Diluted thallium amalgams can be taken as an example of such an effect. As was shown already in [1], at sufficiently negative surface charges, the electric field of the double layer suppresses thallium adsorption at the amalgam/solution interface. As the result, *eg* at [Tl] = 1%, $(\Delta\varphi_{\epsilon=q})_{HgMe}$ is ~0·003 V, whereas the value of $(\Delta\varphi_{\epsilon=0})_{HgMe}$ is 0·19 V[1, 52]. For an amalgam with [Tl] = 10·3% at $(\Delta\varphi_{\epsilon=q})_{HgMe}$ = 0·06 V, whereas $(\Delta\varphi_{\epsilon=0})_{HgMe} = 0{\cdot}32$[1]. The latter value agrees well with $\Delta W_{HgMe} = 0{\cdot}38$ for a 12% Tl amalgam[53]. A similar picture presents itself in the case of indium amalgams[54]. These discrepancies are due to a large difference between the *pzc* value of mercury and those of thallium and indium, which leads to a sharp dependence on potential of the adsorption of thallium and indium at the amalgam/solution interface. Thus, for metal phases of variable composition, the method of elimination of the influence of the term $g_{dip}^{MeH_2O}$ suggested here is in the general case inapplicable (this limitation does not apply to gallium alloys with indium and thallium, since due to the very close values of $\varphi_{\epsilon=0}$ for Ga, In and Tl, the composition of the surface layer should depend little on potential). It is not known as yet whether the electric field of the double layer can affect the electron density distribution in the surface layer, *ie* the value of χ, for individual metals. In principle, such an effect appears possible, although as a rule it is assumed that χ = const at change of ϵ. For further progress in this problem more accurate determinations of the work functions are necessary.

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